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REFLECTION AND REFRACTION OF ATTENUATED WAVES IN SEMI-INFINITE ELASTIC SOLID MEDIA

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Abstract

In earthquakes it is known that waves of one type starting from the origin inside the earth produce waves of other types after impact at the free surface of the earth. A theoretical discussion is given here dealing with reflection and refraction of waves which have their amplitudes increasing with depth similar in nature to the initial diverging earthquake waves which after reflection produce the apparent surface waves in which the displacement decreases with depth. In one case it has been found that at a free surface a plane wave of SV type, travelling parallel to the surface, is capable of generating surface waves after internal reflection which under a certain state of attenuation are identical with the Rayleigh Waves.

The equations of motion of an elastic isotropic solid medium are, in the usual form

$$\rho \frac{\partial^2}{\partial t^2}(u, v, w) = (\lambda+\mu)\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)\Delta + \mu \nabla^2 (u, v, w) \tag{1}$$

and are satisfied by

$$u = \frac{\partial \phi}{\partial x} - \frac{\partial \psi}{\partial z},\ v = v,\ w = \frac{\partial \phi}{\partial z} + \frac{\partial \psi}{\partial x}. \tag{2}$$

if

$$\rho \frac{\partial^2 \phi}{\partial t^2} = (\lambda + 2\mu)\left(\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2}\right) = (\lambda + 2\mu) \nabla^2 \phi$$

$$\rho \frac{\partial^2 \psi}{\partial t^2} = \mu \nabla^2 \psi$$

$$\rho \frac{\partial^2 v}{\partial t^2} = \mu \nabla^2 v \tag{3}$$

Here u, v and w are the components of displacement at any point (x, y, z) at time t, and λ and μ are Lami's constants for the medium in which the wave travels, ρ and Δ the density and dilatation there respectively. The ϕ, ψ and v

denote the movements of dilatational SV and SH type respectively. We will deal with the problem of generation of surface waves by reflection and refraction of other waves by taking the wave-functions in the forms

$$\phi = A \exp i\kappa (x + \alpha z - \omega t)$$
$$\psi = B \exp i\kappa (x + \beta z - \omega t)$$
$$v = C \exp i\kappa (x + \gamma z - \omega t) \tag{4}$$

These forms of solutions assume that the waves are plane and of simple harmonic type. They are propagated with a velocity ω and have a period $2\pi/\kappa\omega$. The motion is assumed to be independent of the y-co-ordinate. The angles of incidence of these waves when they strike a plane $z = \text{const.}$, are $\cot^{-1}\alpha$, $\cot^{-1}\beta$ and $\cot^{-1}\gamma$ respectively. We take the z-axis vertically upwards so that α, β and γ are positive for waves travelling upwards and negative for those travelling downwards.

The conditions of continuity of the transverse horizontal displacement and shearing stress involve only v and not ϕ or ψ. Further, the other four conditions are independent of v. Hence, the six boundary conditions break up into a set of four and a set of two.

(1) u, w, p_{zz}, p_{zx} continuous,

(2) p_{zy}, v continuous.

The former gives only P and SV waves and the latter only SH. We assume that the angles of reflection and incidence are equal to each other.

Impact of an SV at a free surface

Let the free surface of a semi-infinite solid be $z = 0$ and an SV wave strike it from below. After impact the wave gives rise to a reflected ψ and a reflected ϕ wave and we have,

$$\psi = B \exp i\kappa (x + \beta z - \omega t) + B_1 \exp i\kappa (x - \beta z - \omega t)$$
$$\phi = A_1 \exp i\kappa (x - \alpha z - \omega t) \tag{5}$$

If Poisson's condition holds true, the first two equations of (3) give,

$$3\alpha^2 + 2 = \beta^2 \tag{6}$$

Also since the boundary $z = 0$ is a surface of zero stress, we have

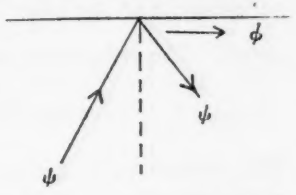
$$p_{zz} = p_{zx} = 0 \tag{7}$$

from which we have,

$$\frac{B}{(1+3\alpha^2)^2 + 4\alpha\beta} = \frac{B_1}{-(1+3\alpha^2)^2 + 4\alpha\beta} = -\frac{A_1}{4\beta(1+3\alpha^2)} \tag{8}$$

Equations (6) give $\beta > \alpha$ or $\cot^{-1}\alpha > \cot^{-1}\beta$, *i.e.*, the angle of reflection of ϕ wave is greater than the angle of incidence of the ψ wave. In the limiting case when the angle of reflection of ϕ wave is 90°, $\alpha = 0$ and the angle of incidence is 35°·25 corresponding to $\beta = \sqrt{2}$.

We will now consider the waves in which the amplitude instead of remaining same at all depths decreases or increases exponentially with the depth z. The propagation of such waves is entirely different from those in which the amplitude remains constant at all depths, which has been discussed by Jeffreys[1] and Knott.[2] Such waves play an important part in the so-called surface waves in which the disturbance dies down with the depth. We shall suppose α, β to be replaced by complex quantities so that,



$$\alpha = \alpha_1 + i\alpha_2, \quad \beta = \beta_1 + i\beta_2 \tag{9}$$

and the relations (5) become

$$\psi = \mathrm{B}\exp\{-\kappa\beta_2 z + i\kappa(x + \beta_1 z - \omega t)\} + \mathrm{B}_1\exp\{\kappa\beta_2 z + i\kappa(x - \beta_1 z - \omega t)\}$$
$$\phi = \mathrm{A}_1\exp\{\kappa\alpha_2 z + i\kappa(x - \alpha_1 z - \omega t) \tag{10}$$

The second of (6) gives

$$3(\alpha_1 + i\alpha_2)^2 = (\beta_1 + i\beta_2)^2 - 2 \tag{11}$$

Then we shall have

$$\beta_1\beta_2 = 3\alpha_1\alpha_2 \tag{12}$$

$$3\alpha_1^2 - 3\alpha_2^2 = \beta_1^2 - \beta_2^2 - 2 \tag{13}$$

Now suppose $\alpha_1 = 0$, *i.e.*, the reflected ϕ wave travels parallel to the surface $z = 0$, then (12) and (13) become

$$\beta_1\beta_2 = 0 \tag{14}$$
$$-3\alpha_2^2 = \beta_1^2 - \beta_2^2 - 2.$$

Two cases arise, when α_2 is finite,

(1) $$\alpha_1 = 0, \ \beta_2 = 0, \ \beta_1 \neq 0 \tag{15}$$

Then $\alpha_2 = \pm\sqrt{\frac{2-\beta_1^2}{3}}$. This imposes the restriction on β_1 that $\beta_1 \leqslant \sqrt{2}$ since α_2 is real. The wave functions take the forms

$$\psi = \mathrm{B}\exp\{i\kappa(x + \beta_1 z - \omega t)\} + \mathrm{B}_1\exp\{i\kappa(x - \beta_1 z - \omega t)\}$$
$$\phi = \mathrm{A}\exp\left\{\sqrt{\frac{2-\beta_1^2}{3}}\kappa z + i\kappa(x - \omega t)\right\} \tag{16}$$

The incident ψ and the reflected ψ waves have their amplitudes same at all depths but the reflected ϕ wave travels parallel to the surface $z=0$ and has two possible amplitudes, one is $A_1 \exp -\sqrt{\frac{2-\beta_1^2}{3}}\,\kappa z$ which increases with the depth and therefore physically impossible from the law of conservation of energy, and the other $A_1 \exp \sqrt{\frac{2-\beta_1^2}{3}}\,\kappa z$ which decreases with the depth. The reflected ϕ wave in this case is given by,

$$\phi = A_1 \exp\left\{\sqrt{\frac{2-\beta_1^2}{3}}\,\kappa z + i\kappa\,(x-\omega t)\right\} \tag{17}$$

The surface wave in this case is wholly dilatational in character and the displacements are given by, after taking the imaginary parts as,

$$u=\frac{\partial\phi}{\partial x}=-\,\kappa A_1\left\{\exp\sqrt{\frac{2-\beta_1^2}{3}}\,\kappa z\right\}\sin\kappa\,(x-\omega t)$$

$$w=\frac{\partial\phi}{\partial z}=\kappa\,A_1\sqrt{\frac{2-\beta_1^2}{3}}\left\{\exp\sqrt{\frac{2-\beta_1^2}{3}}\,\kappa z\right\}\cos\kappa\,(x-\omega t) \tag{18}$$

For such a wave to exist, the angle of incidence of the ψ wave must be less than or equal to $35°\cdot 25$. At the surface $z=0$, the motion of the particles is wholly elliptic and in a retrograde direction. From the equations (3) it can be easily shown that for the ϕ type of wave $\omega^2=(1+\alpha^2)(\lambda+2\mu)/\rho$. Hence after putting $\alpha=\alpha_1+i\alpha_2=i\sqrt{(2-\beta_1^2)/3}$ and assuming that the medium obeys Poisson's condition, the velocity of the wave is found to be

$$\omega=[(1+\beta_1^2)/3]\sqrt{3\mu/\rho} \tag{19}$$

When $\beta_1=\sqrt{2}$, *i.e.*, when the angle of incidence is critical, the z component of displacement vanishes and the x component is

$$u=-\kappa A_1 \sin\kappa\,(x-\omega t) \tag{20}$$

and the wave velocity reduces to $\sqrt{\frac{3\mu}{\rho}}$.

(2) If $\alpha_1=0,\ \beta_1=0,\ \beta_2\neq 0,$ (21)

we have from (13) $\alpha_2=+\sqrt{\frac{\beta_2^2+2}{3}}$, discarding the negative root as before and the ϕ and ψ functions become,

$$\psi = B\exp\{-\kappa\beta_2 z + i\kappa\,(x-\omega t)\} + B_1\exp\{\kappa\beta_2 z + i\kappa\,(x-\omega t)\}$$

$$\phi = A_1\exp\left[\sqrt{\frac{2+\beta_2^2}{3}}\,\kappa z + i\kappa\,(x-\omega t)\right] \tag{22}$$

This case is of special importance as it is favourable for the generation of "Surface Waves of Rayleigh type". The incident ψ wave in which the amplitude increases with depth gives rise to a ψ and a ϕ wave, in both of which the amplitudes decrease with depth. All the waves travel parallel to the boundary $z = 0$.

Relations (8) between the coefficients are,

$$\frac{B}{(1-3\alpha_2^2)^2 - 4\alpha_2\beta_2} = \frac{B_1}{-(1-3\alpha_2^2)^2 - 4\alpha_2\beta_2} = \frac{-A_1}{4i\beta_2(1-3\alpha_2^2)} \tag{23}$$

The equations (22) after neglecting the original ψ part which is incident, and using the above relations, give

$$\psi = \frac{4\alpha_2\beta_2 + (1-3\alpha_2^2)^2}{4\alpha_2\beta_2 - (1-3\alpha_2^2)^2} B \exp[\kappa\beta_2 z + i\kappa(x-\omega t)]$$

$$\phi = i\frac{4\beta_2(1-3\alpha_2^2)^2}{4\alpha_2\beta_2 - (1-3\alpha_2^2)^2} B \exp[\kappa\beta_2 z + i\kappa(x-\omega t)] \tag{24}$$

and if we put

$$b = \frac{4\alpha_2\beta_2 + (1-3\alpha_2^2)^2}{4\alpha_2\beta_2 - (1-3\alpha_2^2)^2} B$$

$$b' = \frac{4\beta_2(1-3\alpha_2^2)}{4\alpha_2\beta_2 - (1-3\alpha_2^2)} B \tag{25}$$

the equations (24) become

$$\psi = b \exp[\kappa\beta_2 z + i\kappa(x-\omega t)]$$

$$\phi = ib' \exp[\kappa\alpha_2 z + i\kappa(x-\omega t)] \tag{26}$$

The components of displacement (u, w) are,

$$u = \frac{\partial\phi}{\partial x} - \frac{\partial\psi}{\partial z} = -[b'\kappa \exp\kappa\alpha_2 z + b\kappa\beta_2 \exp\kappa\beta_2 z] \exp i\kappa(x-\omega t)$$

$$w = \frac{\partial\phi}{\partial z} + \frac{\partial\psi}{\partial x} = i[b'\kappa\alpha_2 \exp\kappa\alpha_2 z + b\kappa \exp\kappa\beta_2 z] \exp i\kappa(x-\omega t) \tag{27}$$

or taking the imaginary parts these become

$$u = -[b'\kappa \exp\kappa\alpha_2 z + b\kappa\beta_2 \exp\kappa\beta_2 z] \sin\kappa(x-\omega t)$$

$$w = -[b'\kappa\alpha_2 \exp\kappa\alpha_2 z + b\kappa \exp\kappa\beta_2 z] \cos\kappa(x-\omega t) \tag{28}$$

At the surface $z = 0$, the motion is elliptic harmonic given by, if ω be replaced by c,

$$u = -[b'\kappa + b\kappa\beta_2] \sin\kappa(x-ct)$$

$$w = -[b'\kappa\alpha_2 + b\kappa] \cos\kappa(x-ct) \tag{29}$$

and the ratio of horizontal to vertical axes is

$$\frac{b' + b\,\beta_2}{b'\,\alpha_2 + b} = \frac{\beta_2\,[4\,(1 - 3\,\alpha_2^2) + 4\,\alpha_2\,\beta_2 + (1 - 3\,\alpha_2^2)^2]}{4\,\alpha_2\,\beta_2\,(1 - 3\,\alpha_2^2) + 4\,\alpha_2\beta_2 + (1 - 3\alpha_2^2)^2} \tag{30}$$

in which $3\alpha_2^2 = \beta_2^2 + 2$.

Now α_2, β_2 must be real and positive so that the displacements may gradually decrease with depth. If the displacements decrease very rapidly α_2 and β_2 are large and the ratio (30) becomes infinite so that there is only horizontal displacement possible.

When β_2 and α_2 are smallest $\beta_2 = 0$, $\alpha_2 = \sqrt{\frac{2}{3}}$ and the attenuation is most gradual and the ratio (30) becomes zero. In this case there is only vertical displacement of the particles.

When $\beta_2 = \alpha_2 = 1$, the limit of the expression in (30) is -1 and the particles describe circles in retrograde direction.

The displacements (28) represent waves of type similar to those of Rayleigh. In particular if the attenuation is such that $\beta_2 = 0{\cdot}3933$, we have from (21) and (19)

$$\alpha_2 = 0{\cdot}8475,\ \omega = 0{\cdot}9194\sqrt{\frac{\mu}{\rho}} = c \tag{31}$$

where c is the velocity of the Rayleigh Waves and putting $r = 0{\cdot}8475\ \kappa$, $s = 0\ 3933\ \kappa$, the equations (28) become

$$u = -\,b'\kappa\left(e^{+rz} + \frac{b}{b'}\,\beta_2\,e^{sz}\right)\sin\kappa\,(x - ct)$$

$$w = -\,b'\kappa\left(\alpha_2\,e^{rz} + \frac{b}{b'}\,e^{sz}\right)\cos\kappa\,(x - ct) \tag{32}$$

Now $b/b' = -1{\cdot}4679$ from (25) and therefore $b\,\beta_2/b' = -0{\cdot}5773$, and (32) becomes

$$u = \mathrm{A}\,[\exp rz - 0{\cdot}5733\,\exp sz]\,\sin\kappa\,(x - ct)$$

$$w = \mathrm{A}\,[0{\cdot}8475\,\exp rz - 1{\cdot}4679\,\exp sz]\,\cos\kappa\,(x - ct) \tag{33}$$

And this is the usual Rayleigh Wave[3] form for the medium for which $\lambda = \mu$. (The z-axis here is taken positive normally away from the medium.) The analysis here shows that whenever there is a plane SV wave of simple harmonic type travelling parallel to the free surface of an elastic solid, and the wave has its amplitude increasing with depth exponentially it generates Rayleigh type of waves in which the amplitude decreases with depth, after internal reflection.

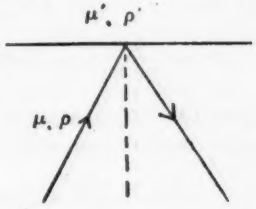
SH-Type.—Let the incident wave be,

$$v = C \exp i\kappa (x - \gamma z - \omega t) \tag{34}$$

Suppose there are two media, in the lower one

$$v = C \exp i\kappa (x + \gamma z - \omega t) + C_1 \exp i\kappa (x - \gamma z - \omega t) \tag{35}$$

and the density and rigidity ρ and μ respectively. In the upper medium the density and rigidity are ρ' and μ' respectively and the refracted ray is,



$$v = C' \exp i\kappa (x + \gamma' z - \omega t) \tag{36}$$

We have as before,

$$\omega^2 = \frac{\mu}{\rho}(1 + \gamma^2) = \frac{\mu'}{\rho'}(1 + \gamma'^2) \tag{37}$$

Since v is continuous at $z = 0$, hence

$$C' = C + C_1 \tag{38}$$

Also $p_{zy} = \mu \dfrac{\partial v}{\partial z}$ is continuous at $z = 0$, hence,

$$\mu\gamma (C - C_1) = \mu'\gamma' C' \tag{39}$$

(38) and (39) give

$$\frac{C}{\mu\gamma + \mu'\gamma'} = \frac{C_1}{\mu\gamma - \mu'\gamma'} = \frac{C'}{2\mu\gamma} \tag{40}$$

Now let $\gamma = \gamma_1 + i\gamma_2$, $\gamma' = \gamma'_1 + i\gamma_2$ (41)

Then (37) and (40) give

$$\mu [1 + \gamma_1^2 - \gamma_2^2]/\rho = \mu' [1 + \gamma_1'^2 - \gamma_2'^2]/\rho' \tag{42}$$

$$\mu \gamma_1\gamma_2/\rho = \mu'\gamma'_1\gamma'_2/\rho' \tag{43}$$

$$\frac{C}{\mu(\gamma_1 + i\gamma_2) + \mu'(\gamma_1' + i\gamma'_2)} = \frac{C_1}{\mu(\gamma_1 + i\gamma_2) - \mu'(\gamma_1' + i\gamma'_2)} = \frac{C'}{2\mu(\gamma_1 + i\gamma_2)} \tag{44}$$

Two cases arise according as $\mu'/\rho' \lesseqgtr \mu/\rho$.

(1) Suppose $\mu'/\rho' < \mu/\rho$, *i.e.*, the velocity in the upper medium is smaller than that below. Also suppose a surface wave is generated in the upper surface, $z = 0$, so that $\gamma_1' = 0$. Then by (43) either γ_1 or γ_2 must vanish.

(*a*) Suppose $\gamma_1' = \gamma_1 = 0$, $\gamma_2 \neq 0$. Then (35) and (36) give,

$$v = C_1 \exp [\kappa \gamma_2 z + i\kappa (x - \omega t)]$$

$$= \frac{\mu\gamma_2 - \mu'\gamma_2'}{\mu\gamma_2 + \mu'\gamma_2'} C \exp [\kappa\gamma_2 z + i\kappa (x - \omega t)]$$

for the lower medium, and for the upper medium,

$$v = \frac{2\mu\gamma_2}{\mu\gamma_2 + \mu'\gamma_2'} C \exp [-\kappa\gamma'_2 z + i\kappa (x - \omega t)]$$

or taking the imaginary parts of these expressions we have for the lower and upper media respectively,

$$v = \frac{\mu\gamma_2 - \mu'\gamma_2'}{\mu\gamma_2 + \mu'\gamma_2'} C [\exp \kappa\gamma_2 z] \sin \kappa (x - \omega t) \tag{45}$$

and $$v = \frac{2\mu\gamma_2}{\mu\gamma_2 + \mu'\gamma'_2} C [\exp -\kappa\gamma'_2 z] \sin \kappa (x - \omega t) \tag{46}$$

Equations (45) and (46) show that if an attenuated SH-wave of type

$$v = C [\exp -\kappa\gamma_2 z] \sin \kappa (x - \omega t) \tag{47}$$

in which the amplitude decreases towards $z = 0$, travels parallel to the surface of discontinuity, it gives rise to a reflected and a refracted surface wave in the lower and upper media given by (45) and (46) in both of which the amplitudes are greatest at $z = 0$, the velocities in the lower and upper media being respectively $\sqrt{\mu (1 - \gamma_2^2)/\rho}$ and $\sqrt{\mu' (1 - \gamma'^2_2)/\rho'}$ (48)

Also since γ_2 and γ'_2 are real, we have the condition imposed upon them that,

$$1 \geqslant \gamma_2 \geqslant 1 - \rho\mu'/\rho'\mu$$

$$1 \geqslant \gamma_2' \geqslant 1 - \mu\rho'/\rho\mu' \tag{49}$$

by virtue of (42), but $\gamma_2' > 0$ physically, and $0 > 1 - \mu\rho'/\mu'\rho$ and therefore

$$1 \geqslant \gamma_2' \geqslant 0.$$

(*b*) Next suppose $\gamma_1' = 0$, $\gamma_2 = 0$, $\gamma_1 \neq 0$. This is the case in which an unattenuated wave impinges obliquely at the surface of discontinuity. The incident wave is

$$v = C \exp i\kappa (x + \gamma_1 z - \omega t) \tag{50}$$

The reflected and refracted waves are,

$$v = C_1 \exp i\kappa (x - \gamma_1 z - \omega t) \tag{51}$$

$$v = C' [\exp i\kappa (x - \omega t)] \exp (-\kappa\gamma_2' z) \tag{52}$$

The conditions (42) give

$$\mu\,(1+\gamma_1{}^2)/\rho=\mu'\,(1-\gamma_2{}'^2)/\rho' \tag{53}$$

and since γ_1 is real, we must have

$$\gamma_2{}'\leqslant\left(1-\frac{\rho'}{\mu'}\cdot\frac{\mu}{\rho}\right)^{\frac{1}{2}} \tag{54}$$

and as the assumption was made that $\mu'/\rho'<\mu/\rho$, this means that γ_2' would be imaginary. A similar argument holds for γ_1 and therefore both the quantities γ_1 and γ_2' do not exist. Our problem then reduces to the reflection and refraction of waves in which the amplitude is same at all depths.

(2) If $\mu'/\rho'>\mu/\rho$, *i.e.*, the velocity is greater in the upper medium, then assuming that a surface wave is generated in the upper medium we have $\gamma_1'=0$ and from (43) either γ_1 or γ_2 must vanish.

(*a*) $\gamma_1'=0$, $\gamma_1=0$. Then as before the waves in the lower and the upper media are

$$v=\frac{\mu\gamma_2-\mu'\gamma_2'}{\mu\gamma_2+\mu'\gamma_2'}\,\mathrm{C}\exp\kappa\gamma_2 z\sin\kappa\,(x-\omega t) \tag{55}$$

and

$$v=\frac{2\,\mu\gamma_2}{\mu\gamma_2+\mu'\gamma'_2}\,\mathrm{C}\exp\,(-\kappa\gamma_2' z)\sin\kappa\,(x-\omega t) \tag{56}$$

Equation (42) gives the relation

$$\mu\,[1-\gamma_2{}^2]/\rho=\mu'\,[1-\gamma_2{}'^2]/\rho' \tag{57}$$

and since γ_2 and γ_2' are real, we have as in (49)

$$1\geqslant\gamma_2\geqslant 1-\rho\mu'/\mu\rho' \tag{58}$$

$$1\geqslant\gamma_2'\geqslant 1-\mu\rho'/\rho\mu' \tag{59}$$

and since $\mu'\rho/\rho'\mu>1$, (58) and (59) hold true. But (58) involves negative values of γ_2 which by (55) shows that if the incident wave has its amplitude decreasing towards $z=0$, the reflected wave has its amplitude increasing towards $z=0$ but the refracted wave (56) has always its amplitude diminishing away from $z=0$, since by (59) γ_2' is always positive.

(*b*) $\gamma_1'=0$, $\gamma_2=0$. The incident, reflected and refracted rays are respectively,

$$v=\mathrm{C}\exp i\kappa\,(x+\gamma_1 z-\omega t) \tag{60}$$

$$v=\mathrm{C}_1\exp i\kappa\,(x-\gamma_1 z-\omega t) \tag{61}$$

$$v=\mathrm{C}'\,[\exp i\kappa\,(x-\omega t)]\exp\,(-\kappa\gamma_2' z) \tag{62}$$

where by (44)

$$\frac{C}{\mu\gamma_1 + i\mu'\gamma_2'} = \frac{C_1}{\mu\gamma_1 - \mu'\gamma_2' i} = \frac{C'}{2\mu\gamma_1} \tag{63}$$

The conditions (42) give

$$\mu(1+\gamma_1^2)/\rho = \mu'(1-\gamma_2'^2)/\rho' \tag{64}$$

and since γ_1 and γ_2' are both real, we must have

$$\gamma_2' \leqslant [1-\rho'\mu/\mu'\rho]^{\frac{1}{2}} \tag{65}$$

$$\gamma_1 \leqslant [(\mu'\rho/\mu\rho') - 1]^{\frac{1}{2}} \tag{66}$$

and since by hypothesis $\mu'/\rho' > \mu/\rho$, these conditions hold good. The reflected and refracted rays are, after taking the imaginary parts of (61) and (62)

$$v = \frac{C}{(\mu\gamma_1)^2 + (\mu'\gamma_2')^2}[\{(\mu\gamma_1)^2 - (\mu'\gamma_2')^2\}\sin\kappa(x - \gamma_1 z - \omega t) - 2\mu\mu'\gamma_1\gamma_2'\cos\kappa(x - \gamma_1 z - \omega t)] \tag{67}$$

$$v = \frac{2\mu C}{(\mu\gamma_1)^2 + (\mu'\gamma_2')^2}[\exp(-k\gamma_2' z)][\mu\gamma_1\sin\kappa(x - \omega t) - \mu'\gamma'_2\cos\kappa(x - \omega t)] \tag{68}$$

Equation (68) gives the surface wave in the upper medium in which the amplitude is maximum at the surface = 0.

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REFERENCES

1. Jeffreys .. *M.N.R.A.S., Geoph. Suppt.* 1, 1926, 321.
2. Knott .. *Phil. Mag.*, 1899, **48**, 64.
3. Jeffreys .. *The Earth.*

EFFECT OF CRYSTAL ORIENTATION ON THE RAMAN EFFECT IN NAPHTHALENE AND BENZOPHENONE

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1. Introduction

It is well known that the benzene molecule is highly anisotropic, the optical and magnetic polarisabilities in the plane of the ring being much larger than those perpendicular to it. A study of this directional variation of the properties of aromatic molecules cannot however be directly made with substances either in the liquid or gaseous condition as the molecules would then have all random orientations. But if such molecules are arranged in a regular manner as they are in a crystal, the crystal as a whole would usually exhibit differences in the polarisability in different directions. The magnitudes of these differences would evidently depend upon the relative orientations of the molecules in the unit cell. When the Raman effect is studied with single crystals of aromatic substances, the changes in the optical polarisation of the molecules due to their hindered rotations and vibrations may be expected also to exhibit anisotropy. We should therefore observe large changes in the intensity of the Raman lines depending upon the orientation of the crystal with respect to the direction of the incident light and that of observation of the scattered light. Except in the case of some inorganic crystals like sodium nitrate (Nedungadi,[1] 1939) and calcite (Bhagavantam,[2] 1940) the effect of crystalline anisotropy on the Raman spectra have not hitherto been demonstrated. This is largely due to the difficulty in getting single crystals of these substances of suitable size and shape for study. The importance of using single crystals in studies of the Raman effect in solids is, however, well recognised. Indeed, unless this is done it is not possible even to record the spectrum completely; the fainter lines and also the strong ones with small frequency shifts being liable to be overlooked. In these circumstances, a study of the Raman effect in single crystals of naphthalene and benzophenone with particular reference to the crystal orientation has been undertaken by the author. The preliminary results obtained are reported in this paper.

2. Anisotropy of naphthalene and benzophenone crystals

The structure of naphthalene has been investigated by K. Banerji[3] (1930) and with especial thoroughness by Robertson[4] (1933). The crystal is monoclinic in the space group C_{2h}^5. The unit cell has the following dimensions:

$$a = 8{\cdot}29 \text{ Å} \qquad b = 5{\cdot}95 \text{ Å} \qquad \text{and} \qquad C = 8{\cdot}68 \text{ Å}$$

$$\angle \beta^* = 122°{\cdot}7$$

The crystal contains two molecules of $C_{10}H_8$

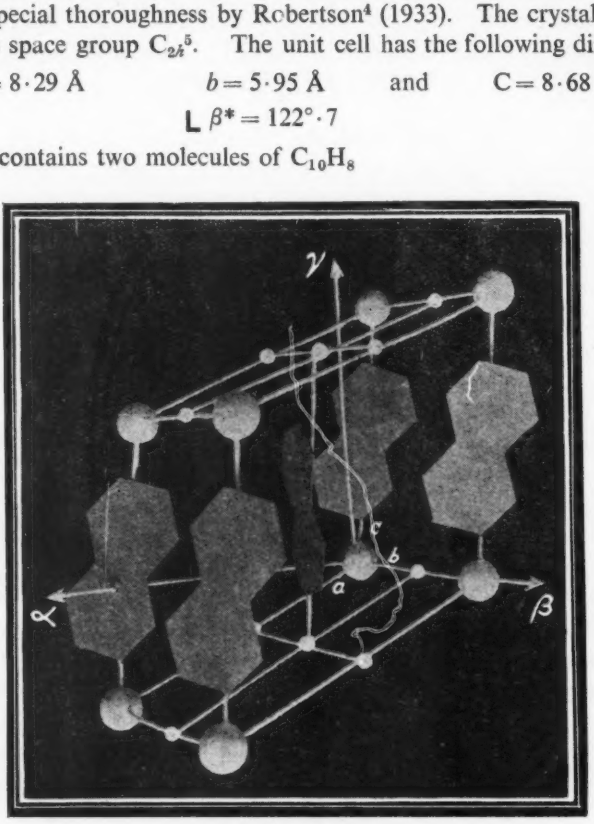


FIG. 1*
Crystal model of naphthalene

The length of the molecule makes angles of 115°·3, 102°·6 and 28°·7 respectively with the *a*, *b* and *c'* (perpendicular to *a* and *b*) whereas the corresponding angles for the breadth of the molecule are 71°·2, 28°·8 and 69°·1. The orientation of the other molecule in the unit cell is obtained by glide plane reflection in the (010) crystal plane, the gliding being parallel to the *a* axis. A photograph of the crystal model of naphthalene made by the

* The balls seen in the Fig. serve only as corner bindings for the frame work and is not part of the lattice.

author showing the orientation of the molecular planes with respect to the crystal axes *a*, *b* and *c* and of the axes of the optical polarisability ellipsoid α, β and γ is shown in Fig. 1. It can be seen that the molecules are not inclined very much with each other, a fact which is evidently the cause for the large optical and magnetic anisotropies observed in the crystal. The latest measurements of Londsdale and Krishnan[5] (1937) for the magnetic susceptibilities of naphthalene and of Sundararajan[6] (1936) for the refractive indices give the following values:

$\chi_2 = -146{\cdot}4 \times 10^{-6}$ e.m.u. $\quad \alpha \rightarrow 1{\cdot}525$

$\chi_3 = -76{\cdot}6 \times 10^{-6}$,, $\quad \beta \rightarrow 1{\cdot}722$

$\chi_1 = -56{\cdot}0 \times 10^{-6}$,, $\quad \gamma \rightarrow 1{\cdot}945$

The crystal being monoclinic, one of the optical axes β and of the magnetic axes χ_3 coincide with the symmetry axis *b* of the crystal and hence along this direction the refractive index and magnetic susceptibility have intermediate values. The other two optical and magnetic axes lie in the (010) plane. The optical axes γ and α are inclined to the *c* axis of the crystal at angles of $9{\cdot}7$ and $99°{\cdot}7$ respectively towards *a*. The magnetic axes χ_1 and χ_2 are inclined at an angle of only $2°{\cdot}3$ to these two optical axes respectively. It may be readily seen that γ is roughly parallel to the length of the molecule along which the optical polarisation is maximum and α is roughly perpendicular to the molecular plane along which the optical polarisation is minimum.

Benzophenone belongs to the rhombic bisphenoidal class with four molecules in the unit cell. No detailed X-ray analysis of the structure of the crystal has hitherto been accomplished and hence, the molecular orientations in the crystal remain unknown. However, it has been established by the studies of Krishnan and his collaborators[7] (1931) that the crystal possesses large diamagnetic anisotropy. This suggests that it should also have large optical anisotropy. Groth[8] remarks that benzophenone is a negative biaxial crystal and has strong double refraction. However, the refractive indices along the three directions α, β, γ (parallel to the crystal axes *c*, *b* and *a* respectively) are not available. Hence, the author has measured these indices by the method of total reflection using a Pulfrich refractometer. The values so obtained as well as the magnetic susceptibilities along *a*, *b* and *c* axes are given below:

$\chi_a = -88{\cdot}0 \times 10^{-6}$ e.m.u. $\quad \gamma \rightarrow 1{\cdot}67$

$\chi_b = -88{\cdot}6 \times 10^{-6}$,, $\quad \beta \rightarrow 1{\cdot}65$

$\chi_c = -149{\cdot}3 \times 10^{-6}$,, $\quad \alpha \rightarrow 1{\cdot}52$

The molecule contains two benzene rings connected through a C=0 group. From the above data we can presume that the benzene rings are nearly parallel to $\beta\gamma$-plane and as a consequence the optical polarisability for light vibrations in this plane is much larger than that for vibrations perpendicular to it.

3. *Experimental*

The single crystals of naphthalene used for the study were prepared from melts of the purified chemical. Carefully regulating the temperature gradient in the furnace large transparent blocks of single crystals could be obtained which on polishing showed strikingly their large double refraction. For studies on the Raman spectra with oriented crystals it is obvious that the crystal has to be cut in the form of a rectangular parallelopiped with edges parallel to the three axes of the optical polarisability ellipsoid (indicatrix) as otherwise complications arise due to double refraction. As the crystal grown from the melt is in the shape of the container, there are no natural faces to guide the fixing of the axes of the crystal. However, the directions of the magnetic axes could be easily determined by orienting the crystal in a strong magnetic field. The optical axis β being coincident with the direction of the intermediate magnetic susceptibility, the α and γ axes were easily determined from their known inclination to the χ_2 and χ_1 axis. The crystal was then cut into the proper shape with its edges (measuring 1·5, 1, 1 cm.) parallel to the optical axes α, β and γ. These directions were further confirmed by observation of the directions of extinction of the crystal between crossed nicols. During the time of exposure the crystal was kept covered by a trace of Canada balsam to avoid the rapid sublimation of the substance.

The crystal of benzophenone available for study was in the form of a thick plate. Fixing the axes on the above principles it was found that the α axis lay in the plane of plate. The thickness of the plate was not large enough to prepare edges of sufficient length along the β and γ axes. However, the anisotropy in the $\beta\gamma$ plane being very small, the study was made with respect to the directions in its plane and perpendicular to it. The crystal was accordingly suitably cut so that an edge measuring about 12 mm. was parallel to the α-axis and a face measuring 15×8 mm. was parallel to the $\beta\gamma$ plane.

As some of the results were concerned with the relative intensities of the Raman lines in different spectrograms, those spectra were to be recorded under strictly identical conditions of the time of exposure, of the depth of illumination of the crystal and the volume of the crystal from which the

scattered light was taken. For this purpose the crystal was contained in a closely fitting brass box with small apertures for the incident and scattered light to pass through. The box was rigidly fixed with respect to the direction of incidence for strictly transverse observation. The crystal orientation inside the box could be then suitably varied to get the various spectrograms.

An accurately oriented polaroid which has an efficiency of 90% in the λ4358 region was used between the condenser and the crystal when the incident light was to be polarised. A Hilger two-prism spectrograph of high light gathering power was employed for the study.

For a comparative study of the characteristics of the spectrum of the melt and of the crystal, the spectrum of benzophenone in the molten state was also taken and the states of polarisation of the Raman lines studied for the first time. The experimental arrangements used in the study of the melt were what are usually employed for the polarisation study of the spectra of liquids.

4. *Results and Discussion*

Frequency shifts in the Raman spectra.—Fig. 2 *a* is a clear and intense spectrum of a single crystal of naphthalene in the form of a cylinder (diameter 2 cms. and length 6 cms.). Fig. 3 gives the spectrum of benzophenone crystal as also the record of the states of polarisation of the Raman lines in the melt. The spectrogram for the crystal in this case is not, however, so intense and good as for the melt due to the slight imperfections of the crystal. Nevertheless, Fig. 3 gives a comparative idea of the spectra of the substance in the solid and liquid states. The study of naphthalene in the molten state was not made in view of the information already available. The results of a careful measurement of these spectrograms are given in Tables I and II together with the relevant data of previous investigators. The intensities recorded in these and subsequent Tables were determined by visual estimate.

The Raman spectrum of naphthalene in the solid state has been examined previously by Anantakrishnan[9] (1937), Canals and Pevrot[10] (1938) as also by Kohlrausch[11] (1938) with crystalline powder using the technique of complementary filters. The most complete spectrum of the melt hitherto reported is that of Saxena[12] (1938) who has also studied the states of polarisation of the Raman lines. The low frequency lattice oscillations have been recorded by Sirkar[13] (1936) and Venkateswaran[14] (1938) with the substance in the form of polycrystalline mass and by Gross and Vuks[15] (1935) with a single crystal. The use of a perfectly clear single crystal has enabled the present author to record the complete spectrum with great intensity and

clearness as is seen in Fig. 2 *a* which is in marked contrast with the spectrograms reproduced by earlier workers. In general, it is found that the four lines due to lattice oscillations are very strong and diffuse as compared to many of the lines due to internal oscillations. In addition to these four lines, 28 internal oscillations have also been recorded in the present study. A perusal of Table I shows that many of them are new. It must be

TABLE I

Naphthalene

Infra-red frequencies (molten)	RAMAN FREQUENCIES				
	Molten (Saxena)	Single crystal (author)	Crystal powder		
			Anantakrishnan	Kohlrausch	Canals and Pevrot
		45 (5)			
		75 (10)			
		107 (7)			
		121 (5)			
	191 (1) D				
	397 (1) D	389 (2)			404 ff
		463 (1)			
623	511 (6) P	512 (10)	511 (3)	513 (6)	518 Ff
714	726 (1) D	724 (1)		728 (1)	702 ff
	760 (6) P	764 (13)	764 (5)	766 (12)	743 ff
782	772 (1) P	784 (1)		786 (1)	764 F
820	941 (2) P	948 (1)*			
881					
961		972 ($\frac{1}{2}$)†			
1000	1024 (5) P	1021 (6)	1019 (5)	1023 (9)	1018 F
		1102 ($\frac{1}{2}$)			1108 ff
1125	1142 (2) D	1143 (3)	1144 (3)	1148 (4)	1144 ff
		1169 (2)	1168 (1)	1168 (2)	
	1206 (0) D	1215 ($\frac{1}{2}$)			1205 f
1220	1239 (1) D	1242 (2)	1240 (2)	1245 (2)	1243 f
	1257 (2) D	1258 ($\frac{1}{2}$)			
1275		1280 (2)	1280 ($\frac{1}{2}$)	1280 (2)	1285 ff
	1326 (1) P	1324 ($\frac{1}{2}$)	1328 (0)	1326 (4)	1322 F
1389	1379 (15) P	1384 (15)	1379 (5)	1384 (20)	1381 FF
	1406 ? (0)				
	1438 (2) D	1442 (1)	1440 (1)	1446 (2)	1436 fF
1492	1460 (4) P	1463 (3)	1460 (5)	1465 (8)	1462 F
		1519 (1)			
	1530 (0) D	1537 ($\frac{1}{2}$)			
1584	1576 (5) D	1576 (7)	1577 (7)	1578 (8)	1576 F
1724		1624 (1)	1623 ($\frac{1}{2}$)	1628 (1)	1626 f
1820					
1940					2980 ff
2380		3000 (1)	3001 (1)		3007 ff
3030		3026 ($\frac{1}{2}$)	3025 (2)		3030 ff
	3058 (4) P	3058 (8)	3054 (12)	3058 (4)	3058 F
		3086 ($\frac{1}{2}$)			
	3244 (2) D				3244 F

* Doublet Structure † Band P Polarised line D Depolarised line

mentioned that a correct assignment of these lines in the spectrum is difficult as some of the C–H valence oscillations excited by λ 4046 and λ 4078 are superposed over other lines excited by λ 4358. Further, confusion is caused in the case of strong spectrograms by the excitation of the intense Raman lines by λ 4339 and λ 4348 of the mercury radiation. Hence, the assignments were made by a careful comparison of three intense spectra taken (1) with a filter of an aqueous solution of sodium nitrite to cut off λ 4046 and λ 4078 from the incident beam; (2) with a filter of iodine in carbon tetrachloride to cut off λ 4358 and (3) without using any filter. In general, the Raman lines in the crystal are extremely sharp. There is good agreement between the frequencies observed in the melt and in the crystal; the shifts of the lines due to change of state are, indeed, quite inappreciable in many cases. All the lines except 191 and 3244 observed in the melt occur in the crystal as well, though there are many lines in the crystal, particularly in the region of the C–H valence oscillation, which do not occur in the melt. The line 191 is perhaps characteristic of the molten state of naphthalene. The genuineness of the line 3244 recorded by Saxena in the melt and by Canals and Pevrot in the crystal is doubtful as the λ 4046 excitation of it cannot be separated from λ 4078 excitation of the strong line 3058. Further, no corresponding line is observed in the λ 4358 excitation. The frequencies reported by Canals and Pevrot are in many cases very much divergent from those of other investigators.

From the structural formula of naphthalene Kohlrausch[16] (1935) and Bonino[17] (1936) have discussed the symmetry of the molecule and have established that it has the symmetry D_{2h}. Accordingly the molecule should have 48 modes of oscillation out of which 24 are active in Raman effect, 20 in infra-red and 4 inactive in both. 20 frequencies in Raman effect and 18 in infra-red (Le Compte,[18] 1933) have actually been observed in the melt and as none of the infra-red active frequencies coincides with any of the Raman active frequencies, it is concluded that the molecule has a centre of symmetry consistent with the symmetry D_{2h} of the molecule. Polarisation studies of the Raman lines in the spectrum of the melt have further confirmed this structure. Now, when a group of atoms constituting the molecule enters the unit cell of a crystal, its normal modes will, in general, undergo modification in three directions. The first one is the splitting of the degenerate modes due to degradation of symmetry. Though the naphthalene molecule enters a less symmetrical monoclinic lattice with symmetry C_{2v} there is no splitting of any frequency on this account as the molecule has no degenerate modes. However multiplication of the lines can take place by having more than one molecule in the unit cell, as is the

case with naphthalene. A third modification is in the matter of selection rules according to which infra-red active and Raman inactive oscillations of the molecule may become active in Raman effect and *vice versa*. The close agreement of the infra-red active frequencies namely 3030, 1389, 1275 and 782 with the Raman active frequencies 3026, 1384, 1280 and 784 respectively suggest this possibility. The large number of lines observed in the spectrum of the crystal is then due to the above two causes. Detailed analyses of the modes of oscillation of the naphthalene molecule and of the crystal on the lines of the analyses already available in the case of the benzene molecule would be of particular interest though they are difficult due to the large number of atoms contained in the molecule.

In Table II are given the data for benzophenone in the crystalline and molten states. In the case of the crystal the intensities recorded are for the case in which the unpolarised light is incident in the $\beta\gamma$ plane, the observation being perpendicular to it. The compound being lightly yellow in colour, λ 4046 was partly absorbed and hence, λ 4358 was used as the exciting radiation. As a consequence the C–H valence oscillation excited by λ 4046 was recorded only weakly.

TABLE II

Benzophenone λ 4358 *excitation*

Raman lines in the crystal		Raman lines in the melt			Raman lines in the crystal		Raman lines in the melt		
Frequency	Intensity	Frequency	Intensity	State of polarisation	Frequency	Intensity	Frequency	Intensity	State of polarisation
60	6				862	1	849	2 *d*	P
100	5				999	10	1000	10	P
122	4				1027	5	1025	5	P
148	1 *d*	149	5 *d*	D	1151	8	1148†	10 *d*	P
218	4	215	8 *d*	D	1160*	1	1159*	0	P
294*	1	291	3	P			1275	4	D
		396*	2	D			1312	1	D
407*	2	408	2	D			1383	0	D
432*	1	433*	1	P	1457	1	1446	2	P
563	2	563	5	P	1485	1	1489	2	P
613	3	614	6	D			1587*	1	P
		633*	1	D	1596	15	1597	15 *d*	D
721	3	716	5	P	1650	10	1660	11 *d*	P
766	1	761	4	P			1708*	2 *d*	D
		807	1	D	3051	2 *k*	3056	7 *d*	P

k λ 4046 excitation
P Polarised lines, $\rho << \cdot 86$
D Depolarised line $\rho = \cdot 86$
d Diffuse
† Doublet structure
* Lines observed for the first time

The Raman spectrum of benzophenone has previously been studied in the molten state by Dadieu and Kohlrausch[19] (1929), Thatte and Joglekar[20] (1935) as well as by Kohlrausch and Pongratz[21] (1934) and with a polycrystalline mass by Krishnamurti[22] (1930) Venkateswaran[14] (1938) and also by Gupta[23] (1938). In the present study besides recording all the lines hitherto reported by these workers some new lines indicated in the Table are also observed both in the crystal and in the melt. It can be said, in general, that the lines in the solid are somewhat sharper than in the liquid. In passing from the liquid to the solid state, the Raman lines show only inappreciable changes in frequency except in the case of the lines 849, 1446 and 1660. The low frequency lattice oscillations in the crystal are replaced by an intense wing on either side of the Rayleigh line, the extension of which sharply ends at the last lattice line in the crystal. The great intensity of the wing is readily understood from the great anisotropy of the molecule. In the spectrum of the melt 27 Raman frequencies are observed out of which 15 lines are polarised and the rest depolarised. Due to the complicated nature of the molecule it is difficult to attribute with any degree of certainty all the lines observed to definite modes of oscillation of the molecule. However it is obvious that the most intense line in the spectrum of the melt 1597 is due to the C = C oscillation of the molecule and the strong line 1660 is due to the C = O of the ketone group. It is known, however, that in many ketones, aldehydes and esters, the carbonyl frequency occurs above 1700. It appears therefore that the new line 1708 observed is also due to the C = O linkage. It might be expected that this doubling of the carbonyl frequency is an effect of polymerisation, a property of the melt indicated by its tendency to remain a super-cooled liquid below the melting point.

Effect of crystal orientation on the Raman spectra.—As is usual in studies of the effect of crystal orientation on its spectrum, we designate the direction of the incident beam of light by OX, that of observation by OY, the OZ being perpendicular to both. Numerous spectra can be got by varying the orientation of the crystal relatively to the directions of the incident and scattered beams and those of the vibrations of the incident light vector. Only a few of these spectra have been taken in the present case. Spectra *b* and *c* of Fig. 2 and Fig. 4 illustrate the orientation effect in naphthalene and Fig. 5 that in benzophenone. As the relative intensities in the spectra in each Figure are to be compared, the spectrograms seen in any particular figure were recorded on the same plate under identical experimental conditions and printed simultaneously on the same paper, the crystal orientation being, however, different. In these spectra the weak lines reported in the previous section have not all been recorded. Further, when the polaroid

is placed in the incident beam, the C–H lines due to the λ 4046 are recorded only weakly as the exciting line is partly absorbed by them. The relative intensities of the lines in these spectra are recorded in Tables III, IV and V.

As has already been remarked we must expect that the polarisation of the molecule when an incident electric vector vibrates in the plane of the ring should be much larger than when it vibrates perpendicular to the plane. This anisotropy will have a large influence on the planar vibrations of the molecule namely that the Raman lines corresponding to these oscillations should be excited more strongly in the former case than in the latter. This is, indeed, the fact as can be seen in Figs. 2 *b* and 2 *c* both of which were taken with unpolarised incident light. In the former the $\beta\gamma$ plane of the crystal is coincident with the YZ plane with γ parallel to OZ, whereas in the latter the $\alpha\gamma$ plane coincides with YZ with α along OZ. In Fig. 2 *b* many of the Raman lines due to the internal oscillations are strong while in Fig. 2 *c* they are weak. This is readily understood since, as has already been remarked, the γ direction is approximately parallel to the length of the molecule and the α direction is normal to the molecular plane. This change in intensity of the lines is quite conspicuous in spite of the fact that the OY component of the incident light, though along the direction of observation contributes more in the latter case than in the former to the total intensities of these spectra. From Table III it can be seen that the line 1384 due to the symmetrical " breathing oscillation " of the ring has, in fact, more than double the intensity in the former case compared to the latter. The internal oscillations 512, 764, 1021, 1143, 1242, 1384, 1442, 1463 and 3058 show the above change in intensity in a striking manner. It can be therefore concluded that these should correspond to some of the 17 planar vibrations of the molecule.

The above effects are still more striking in Figs. 4 *a*, 4 *b* and 4 *c* in all of which the incident light is polarised with vibrations along OZ; but the three optical axes are respectively oriented parallel to OZ. It can be seen that when the incident light vector is along γ the direction of maximum optical polarisability the Raman lines are quite strong (Fig. 4 *a*). When it is parallel to β along which the optical polarisability has the intermediate value (Fig. 4 *b*) the Raman lines are weaker. However, when it is along α the direction of minimum optical polarisability (Fig. 4 *c*), the lines are weakest. It should be remarked that not all the lines in the spectrum behave in the above manner. As an example may be cited the line 1576 (generally attributed to the C = C oscillation) as it is strongly excited only when the incident electric vector is parallel to the β axis. Further, it is found that even when the incident light vector is in the direction of observation

TABLE III

Naphthalene (Incident light unpolarised)

Illuminating beam along OX, observation along OY

Ref. to Fig.	Orientation of the β-axis along	Orientation of the α-axis along	Incident light vibrations in	Intensities of Raman Lines														
				45	75	107	121	389	512	764	1021	1143	1169	1242	1384	1442	1463	1576	3058
2 *b*	OY	OX	YZ plane	6	12	5	5	1	9	7	5	2	0	2	15	2	5	3	9
2 *c*	OY	OZ	YZ plane	3	12	9	8	1	3	3	2	1	1	1	6	1	1	3	4

TABLE IV

Naphthalene (Incident light polarised)

Illuminating beam along OX, observation along OY

Ref. to Fig.	Orientation of the β-axis along	Orientation of the α-axis along	Incident light vibrations along	Intensities of Raman Lines										
				45	75	107	121	512	764	1021	1384	1463	1576	3058
4 *a*	OY	OX	OZ	3	15	2	1	6	5	4	13	4	1	2
4 *b*	OZ	OY	OZ	5	7	6	5	2	6	2	9	1	5	1
4 *c*	OY	OZ	OZ	1	16	8	7	2	2	1	5	1	1	0
	OY	OX	OY	8	10	1	4	2	2	1	7	1	2	1
	OZ	OY	OY	2	15	1	3	1	1	0	3	1	1	0

TABLE V

Benzophenone (Incident light polarised)

Illuminating beam along OX, observation along OY

Ref. to Fig.	Orientation of the $\beta\gamma$ plane	Incident light vibrations along	Intensities of Raman Lines																
			60	100	122	148	218	294	407	563	613	721	766	999	1027	1151	1596	1650	3051
5 *a*	‖to XZ plane	OZ	4	8	6	1	4	1	3	1	3	3	1	9	5	8	15	11	2
5 *b*	‖ to XY plane	OZ	7	11	5	0	5	0	0	0	1	1	0	7	2	3	6	4	1
5 *c*	‖ to XY plane	OY	6	8	5	1	4	0	0	1	3	2	1	8	3	6	13	8	1
5 *d*	‖ to XZ plane	OY	7	5	3	0	3	0	0	0	1	1	0	3	1	2	4	3	1

(Table IV, row 4) many of the lines appear though weakly. The weakest spectrum is, as may be expected, when the direction of observation and the incident light vector coincide with α the direction of minimum optical polarisability.

This influence of the anisotropy of the crystal on the intensity of the Raman lines is strikingly seen also in the case of benzophenone. For both spectrograms 5 *a* and 5 *b* the incident light vector is perpendicular to the direction of observation; but the orientations of the crystal are different. In Fig. 5 *a* where the incident light vector is in the $\beta\gamma$ plane some of the Raman lines particularly those with frequency shifts 1151, 1596 and 1650 are strong, whereas in Fig. 5 *b* when the incident light vector is perpendicular to the above plane, these lines are very weak. The same is true of Figs. 5 *c* and 5 *d* in both of which the incident light vector is along the direction of observation; however, in the former the electric vector is in the $\beta\gamma$ plane and in the latter it is perpendicular to this plane. Comparing Figs. 5 *a* and 5 *c* in both of which the incident light vector is in the $\beta\gamma$ plane, the latter is the weaker as in this case the direction of observation coincides with the direction of the light vibrations. For similar reasons Fig. 5 *d* is weaker than 5 *b*. However there are some lines in the spectrum like 218 which do not show any marked change in the intensity with orientation.

In the case of both crystals, especially in naphthalene, it is found that lines which conspicuously change in intensity with orientation occur as polarised lines in the spectrum of the molten substance. However, some lines which are depolarised in the liquid are also found to fluctuate in intensity though to a less marked extent in the crystal.

From the above observations it is clear that the behaviour of the Raman lines characteristic of naphthalene and benzophenone molecules are in good agreement with what is expected from the known orientation of the molecules in the crystal and its observed optical anisotropy.

The low frequency lattice oscillations show the most varied characteristics as the orientations of the crystals are changed with respect to the direction of vibration of the incident light and that of observation of the scattered light. The four lattice lines in naphthalene behave differently relative to each other. The lines 107 and 121 are weak in Fig. 2 *b* when the internal oscillations are strong while they are intense in Fig. 2 *c* when the internal oscillations are weak. This reciprocal behaviour is also seen in Figs. 4 *a*, 4 *b* and 4 *c*. However, in spite of this analogous behaviour of these two lines, their relative intensities change markedly as can be seen in Table IV. The strongest line 75 is excited strongly by light vibrations along α and γ

and only weakly by that along β. The behaviour of this line is therefore reciprocal to that of the internal oscillation 1576. The line 45 also undergoes large changes of intensity with orientation; however, its behaviour is generally different from that of the other three lines.

In benzophenone also the reciprocal behaviour is seen in the increased intensity of the low frequency lines 60 and 100 as one passes from Fig. 5 *a* where the internal oscillations are strong to Fig. 5 *b* where they are weak. The third line 122, however, correspondingly decreases in intensity. The relative intensities of these three lines alter notably in Figs. 5 *c* and 5 *d*.

It is obvious that when optically anisotropic molecules such as the ones that have been studied here go to make up a crystal lattice, these molecules should be capable of executing rotational oscillations which appear as low frequency lines in the spectrum. From the reciprocal behaviour of the lines 107 and 121 of naphthalene and 60 and 100 of benzophenone with the internal oscillations it is reasonable to conclude that these lines are due to tilting oscillations of the molecules in the lattice. Analogous observations have already been made in the case of sodium nitrate (Raman and Nedungadi,[24] 1939). A careful and detailed study of these crystals afford the prospect of identifying the exact modes of oscillations of the crystal lattices giving rise to these low frequency lines. Such a quantitative study of a large single cyrstal of naphthalene in order to get information about the polarisability tensors responsible for the various oscillations appearing in the spectrum is in progress and the results will be published in due course.

Finally, the author wishes to record his deep sense of gratitude to Professor Sir C. V. Raman for his keen interest in the present work.

5. *Summary*

The paper reports the results of a careful study of the Raman spectra of single crystals of naphthalene and benzophenone, as well as a polarisation study of benzophenone in the molten state. 4 lattice and 28 internal oscillations have been observed in naphthalene the frequency shifts being 45, 75, 107, 121, *389*, *463*, 512, 724, 764, 784, 948, *972*, 1021, 1102, 1143, 1169, *1215*, 1242, *1258*, 1280, 1324, 1384, 1442, 1463, *1519*, *1537*, 1576, 1624, 3000, 3026, 3058 and *3086*. 22 lines including 3 " lattice lines " have been recorded in benzophenone crystal and 27 lines in its melt out of which 15 lines are polarised and 12 are depolarised. Among these, the lines in *italics* in naphthalene, the lines 294, 407, 432 and 1160 in benzophenone crystal, and the lines 396, 433, 633, 1159, 1587 and 1708 in benzophenone melt have been observed for the first time. Further, a study has been made

of the effect of orientation of the above crystals on their Raman spectra. Remarkable changes on the intensities of some of the Raman lines are observed depending upon the orientation of the crystal with respect to the directions of incidence and observation and different states of polarisation of the incident light. From the observed changes in intensities and the known molecular orientations in the crystal, it is deduced that the incident light vector vibrating in the plane of the aromatic ring excites some oscillations of the molecules much more strongly than the light vector perpendicular to the plane. The frequencies in naphthalene which conspicuously change in intensity with orientation namely 512, 764, 1021, 1143, 1242, 1384, 1442, 1463 and 3058 are identified as some of the 17 planar oscillations of the molecule. The lines due to the lattice oscillations also undergo large changes in intensity with orientation. The lines 107 and 121 in naphthalene as also 60 and 100 in benzophenone behave in a reciprocal manner to many of the internal oscillations, *i.e.*, the former appear strongly when the latter are weak and *vice versa*. The behaviour of the strong lattice frequency 75 in naphthalene is, however, reciprocal to that of the internal oscillation 1576.

REFERENCES

1. Nedungadi .. *Proc. Ind. Acad. Sci.*, 1939, **10**, 197.
2. Bhagavantam .. *Ibid.*, 1940, **11**, 189.
3. Banerji, K. .. *Ind. J. of Physics*, 1930, **4**, 557.
4. Robertson .. *Proc. Roy. Soc.*, 1933, **142**, 674.
5. Londsdale and Krishnan .. *Ibid.*, 1936, **156**, 109.
6. Sundararajan .. *Zeit. f. Krist.*, 1936, **93**, 238.
7. Krishnan, Guha and Banerji *Phil. Trans. Roy. Soc.*, 1933, **231**, 235.
8. Groth .. *Chemiche Kristallographe*, Vol. 5.
9. Anantakrishnan .. *Proc. Ind. Acad. Sci.*, (A), 1937, **5**, 200.
10. Canals and Pevrot .. *Comptes Rendus*, 1937, **206**, 119.
11. Kohlrausch .. *Zeit. f. Phy. Chem.*, 1938, **39**, 431.
12. Saxena .. *Proc. Ind. Acad. Sci.*, 1938, **8**, 73.
13. Sirkar .. *Ind. J. Physics*, 1936, **10**,109.
14. Venkateswaran .. *Proc. Ind. Acad. Sci.*, 1938, **8**, 448.
15. Gross and Vuks .. *J. Phy. radium*, 1936, **7**, 113.
16. Kohlrausch .. *Berichte*, 1935, **68** B, 893.
17. Bonino .. *Gazz. Chim. ital.*, 1936, **66**, 827.
18. Le Comte .. *Pob. Sc. et. Tech. du Ministere de l'Air*, Paris (1933).

19. Dadieu and Kohlrausch .. *Monatsch*, 1929, **53–54,** 282.
20. Thatte and Joglekar .. *Phil. Mag.*, 1935, **19,** 116.
21. Kohlrausch and Pongratz *Monatsch*, 1934, **64,** 374.
22. Krishnamurti .. *Nature*,1930, **125**,463.
23. Gupta .. *Ind.J. of Physics*, 1938, **12,** 355.
24. Raman and Nedungadi .. *Nature*, 1939, **153,** 679.

RAMAN SPECTRA WITH UNPOLARISED INCIDENT LIGHT

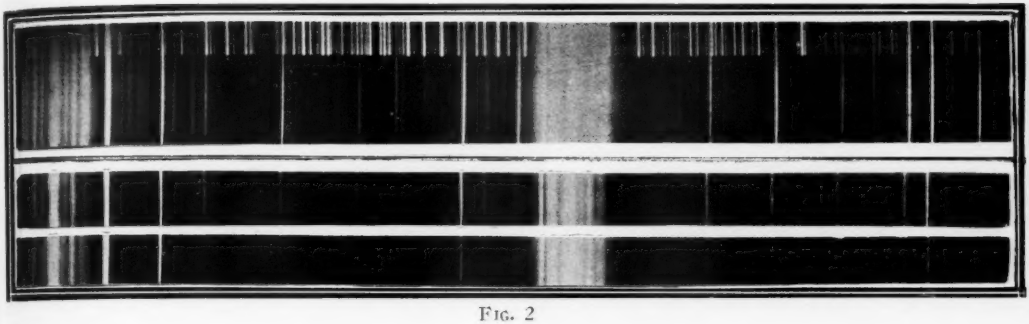


FIG. 2

(*a*) Naphthalene crystal (unknown orientation)
(*b*) ,, ,, Incident light vibrations in the $\beta\gamma$ plane, observation along β
(*c*) ,, ,, ,, ,, $\alpha\gamma$,, ,, γ

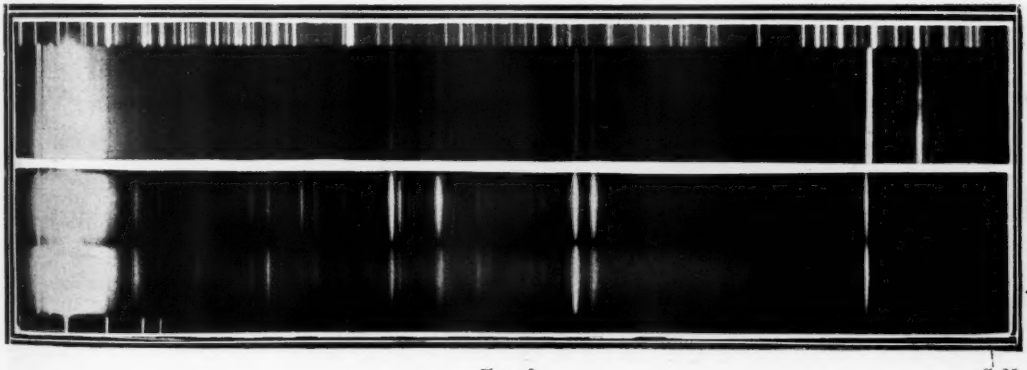
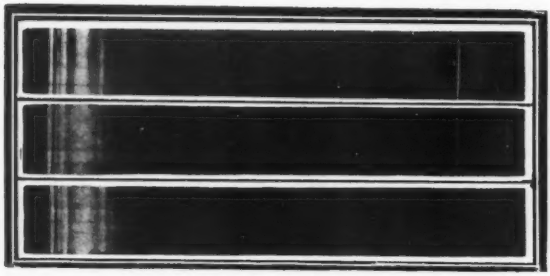


FIG. 3

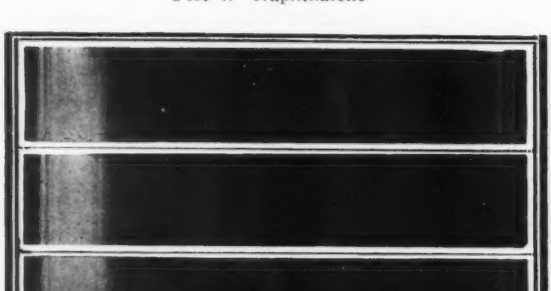
(*a*) Benzophenone crystal
(*b*) ,, melt

RAMAN SPECTRA WITH POLARISED INCIDENT LIGHT



	I.L.V. along	Observation along
a	γ	β
b	β	a
c	a	β

FIG. 4. Naphthalene



	I.L.V. along	Observation along
a	$\beta\gamma$	$\perp$ to I.L.V.
b	a	$\beta\gamma$
c	$\beta\gamma$	$\parallel$ to I.L.V.
d	a	a

FIG. 5. Benzophenone

HETEROCYCLIC COMPOUNDS

Part XII. Chromones from Resacyl and Gallacylphenones Containing Long-Chain Acylgroups, and Some Chemical Properties of these Hydroxy-Ketones

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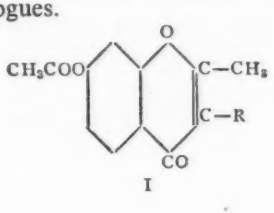
Received October 4, 1940

IN the preceding paper[1] we have shown that the chromones from 2-stearyl- and 2-palmityl-1-naphthols behave differently from the usual chromones, as their alkaline hydrolysis gives exclusively the original ketones unaccompanied by any trace of 1-hydroxy-2-naphthoic acid. As this observation was sufficiently interesting to merit further work, we decided to prepare the chromones from 4-stearyl- and 4-palmityl-resorcinols, as well as 4-stearyl- and 4-palmityl pyrogallols, and to study their alkaline hydrolysis. The second interesting point that could be tested was the generalisation of Heilbron and co-workers[2] that during the Kostanecki acylation of *o*-hydroxy-acylphenones, the formation of the chromones would be promoted by the acyl groups containing long-chain alkyl groups.

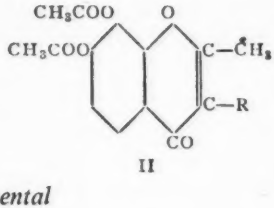
2-Stearyl- and 2-Palmityl-resorcinols were prepared in good yield by the usual Nencki Process. Acetylation of these ketones in presence of anhydrous sodium acetate gave exclusively 2-methyl-3-hexadecyl-7-acetoxychromone (I, R = $C_{16}H_{33}$)- and 2-methyl-3-tetradecyl-7-acetoxychromone (I, R = $C_{14}H_{29}$), no trace of the isomeric coumarins being formed. The alkaline hydrolysis of these chromones gave 4-stearyl-resorcinol and 4-palmitylresorcinol respectively. Similarly stearic and palmitic acids gave 4-stearyl- and 4-palmityl-pyrogallols with pyrogallol. These ketones also gave entirely the chromones on subjecting to the Kostanecki Reaction. 7: 8-diacetoxy-2-methyl-3-hexadecylchromone (II, R = $C_{16}H_{33}$) and 7: 8-diacetoxy-2-methyl-3-tetradecylchromone (II, R = $C_{14}H_{29}$) gave also, on alkaline hydrolysis, 4-stearyl- and 4-palmityl-pyrogallols. Thus these benzo-γ-pyrones as well as the naphtha-γ-pyrones described before, behave in an identical manner on hydrolysis. Moreover, Heilbron and co-workers' generalisation regarding the formation of chromones is amply borne out.

As these interesting ketones were prepared for the first time, we studied their bromination, nitration and Clemmensen Reduction. During bromination and nitration, it was not possible to introduce more than one

bromo- or nitro-groups, where as the reverse was the case with regard to resacetophenone and gallacetophenone. Klarmann[3] has described the preparation of 4-laurylresorcinol, but did not study its properties. We have studied not only its properties but also prepared 4-lauryl-pyrogallol and subjected it to bromination, nitration, reduction, etc., and find that these lauryl derivatives simulate the behaviour of their stearyl- and palmityl-analogues.



I



II

Experimental

(*A*) *Condensation of Resorcinol with Stearic, Palmitic and Lauric Acids*

Preparation of 4-*Stearyl-resorcinol.*—An intimate mixture of dry resorcinol (20 g.), stearic acid (30 g.) and powdered anhydrous zinc chloride (20 g.) was heated in an oil-bath at 150° for three hours. The cooled reaction mixture was first treated with water containing hydrochloric acid, then with a dilute solution of sodium bicarbonate, and finally with 5 per cent. sodium hydroxide solution which dissolved almost everything. The filtered solution, on acidification with concentrated hydrochloric acid, gave a brownish-yellow solid which crystallised from alcohol in lustrous flat needles, m.p. 89–90°. (Yield = 70 per cent.)

4-*Stearyl-resorcinol* was soluble in the usual organic solvents and its alcoholic solution gave red coloration with ferric chloride. (Found: C, 76·4; H, 10·7. $C_{24}H_{40}O_3$ requires C, 76·6; H, 10·6 per cent.)

The p-*Nitrophenylhydrazone* was prepared by heating the mixture of the ketone (0·5 g.), *p*-nitrophenylhydrazine (0·5 g.) and alcohol (20 c.c.) under reflux for five hours, and crystallised from the same solvent in small reddish flakes, m.p. 95–96° (depressed to 68° by the original ketone). (Found: N, 8·3. $C_3OH_{45}N_3$ requires N, 8·2 per cent.)

Kostanecki Reaction with 4-*Stearyl-resorcinol and Preparation of* 7-*Acetoxy*-2-*methyl*-3-*hexadecyl-chromone.*—The mixture of the ketone (2 g.), anhydrous sodium acetate (2 g.) and acetic anhydride (12 c.c.) after being heated in an oil-bath at 175–80° for 14 hours, was poured into water. The white substance that separated out crystallised from alcohol in white, shining needles, m.p. 82–83° (depressed to 62–63° by the original ketone). It was soluble in the usual organic solvents, insoluble in dilute alkali solution

and dissolved in concentrated sulphuric acid giving a reddish-orange colour. (Yield = 70 per cent.) (Found: C, 76·2; H, 9·7. $C_{28}H_{42}O_4$ requires C, 76·0; H, 9·5 per cent.)

Hydrolysis of the above Chromone to 4-*Stearylresorcinol.*—A suspension of the chromone (0·5 g.) in 5 per cent. sodium hydroxide solution (15 c.c.) was heated on sand-bath under reflux for three hours. The filtered solution, on acidification with concentrated hydrochloric acid gave a solid which was identified as 4-stearyl-resorcinol by mixed m.p. with the authentic specimen.

Bromination of 4-*Stearyl-resorcinol to* 6-*Bromo-*4-*stearyl-resorcinol.*—Bromine (0·2 c.c.) dissolved in glacial acetic acid (5 c.c.) was gradually added to the solution of the ketone (1·5 g.) in glacial acetic acid (25 c.c.), and the mixture was poured into much water after 24 hours. The solid crystallised from alcohol in flat needles, m.p. 98–99°. It was not affected by heating with an alkali solution. As the β-substitution is usual in the resorcinol derivatives, it has been assumed that the bromine has occupied the 6-position in the nucleus. (Found: Br, 17·4. $C_{24}H_{39}O_3Br$ requires Br, 17·6 per cent.)

This monobromo-derivative could not be further brominated.

6-*Nitro-*4-*Stearyl-resorcinol.*—A glacial acetic acid solution (10 c.c.) of fuming nitric of $d. = 1·5$ (0·2 c.c.) was gradually added to the solution of the ketone (1·5 g.) in glacial acetic acid (30 c.c.). The precipitate obtained by diluting the mixture with much water after 24 hours crystallised from alcohol in yellowish-white needles, m.p. 97–98°. It could not be further nitrated, and was not affected by heating with alkali solution. (Found: N, 3·25. $C_{24}H_{39}O_5N$ requires N, 3·3 per cent.)

Clemmensen Reduction to 4-*Octadecyl-resorcinol.*—A mixture of the ketone (2 g.), amalgamated zinc (7 g.), dilute hydrochloric acid (30 c.c.) and alcohol (10 c.c.) was heated on sand-bath under reflux for eight hours. The reduction product isolated by extracting the mixture with ether crystallised from alcohol in white, lustrous needles, m.p. 83–84° (depressed to 66–68° by the original ketone). It was soluble in the kusual organic solvents, and its alcoholic solution did not give any coloration with ferric chloride. (Found: C, 79·3; H, 11·7. $C_{24}H_{42}O_2$ requires C, 79·6; H, 11·6 per cent.)

4-*Palmityl-resorcinol* prepared by the usual method from palmitic acid (28 g.), dry resorcinol (20 g.) and anhydrous zinc chloride (20 g.) in 75 per cent. yield crystallised from alcohol in yellowish, lustrous flakes, m.p. 89–90°. Its alcoholic solution gave red coloration with ferric chloride. (Found: C, 75·7; H, 10·4. $C_{22}H_{36}O_3$ requires C, 75·9; H, 10·4 per cent.)

6-*Bromo*-4-*palmityl-resorcinol* crystallised from alcohol in small, white needles, m.p. 92–93° (depressed to 70–71° by the original ketone.) It was not affected by heating with an alkali solution, and could not be further brominated. (Found: Br, 18·7. $C_{22}H_{35}O_3Br$ requires Br, 18·8 per cent.)

The p-*Nitrophenylhydrazone* of 4-palmityl-resorcinol crystallised from alcohol in orange needles, m.p. 94-95°. (Found: N, 8·6. $C_{28}H_{41}O_4N_3$ requires N, 8·7 per cent.)

7-*Acetoxy*-2-*methyl*-3-*tetradecyl-chromone* crystallised from hexane in brown, flat needles m.p. 93–94°. It was insoluble in alkali solution but was soluble in the usual organic solvents. Its solution in concentrated sulphuric acid was yellowish-green in colour. (Yield = 65 per cent.) (Found: C, 75·2; H, 9·5. $C_{26}H_{38}O_4$ requires C, 75·4; H, 9·2 per cent.)

On alkaline hydrolysis, it was converted into 4-palmityl-resorcinol.

6-*Nitro*-4-*palmityl-resorcinol* crystallised from alcohol in yellowish, shining needles, m.p. 97–98°. (Found: N, 3·5. $C_{22}H_{35}O_5N$ requires N, 3·6 per cent.)

4-*Hexadecylresorcinol* crystallised from hexane in brown, shining flakes, m.p. 86–87° (depressed to 72° by the original ketone). Its alcoholic solution did not give any coloration with ferric chloride. (Found: C, 78·8; H, 11·5. $C_{22}H_{38}O_2$ requires C, 79·1; H, 11·4 per cent.)

4-*Laurylresorcinol* was prepared as usual in 70 per cent. yield from lauric acid. It crystallised from hexane in small needles, m.p. 74°. Its alcoholic solution gave red colour with ferric chloride solution. (Found: C, 73·8; H, 9·8. Calc. for $C_{18}H_{28}O_3$ C, 74·0; H, 9·6 per cent.)

The p-*Nitrophenylhydrazone* crystallised from alcohol in deep red lustrous needles, m.p. 86–87°. (Found: N, 9·7. $C_{24}H_{33}O_4N_3$ requires N, 9·8 per cent.)

6-*Bromo*-4-*laurylresorcinol* crystallised from alcohol in white, lustrous flakes, m.p. 84–85°. It was not affected by heating with alkali, neither could it be further brominated. (Found: Br, 21·4. $C_{18}H_{27}O_3$ Br requires Br, 21·5 per cent.)

4-*Dodecyl-resorcinol* crystallised from benzene in reddish-brown needles, m.p. 137–38°. It was not readily soluble in hexane. (Found: C, 77·5; H, 10·6. $C_{18}H_{30}O_2$ requires C, 77·7; H, 10·8 per cent.)

(*B*) *Condensation of Pyrogallol with Stearic, Palmitic and Lauric Acids*

General Remarks.—It was necessary to heat the mixture of pyrogallol with fatty acids only for two hours to get the best yield. Addition of

small quantities of sodium bisulphite had a beneficial effect as it prevented the discoloration of the products. Other details have been omitted as they do not differ essentially from those of the preparation of resorcinol analogues.

4-*Stearyl-pyrogallol* obtained in 75 per cent. yield was soluble in most of the organic solvents and crystallised from alcohol in small, lustrous needles, m.p. 80–81°. Its alcoholic solution gave violet coloration with ferric chloride. (Found: C, 73·3; H, 10·3. $C_{24}H_{40}O_4$ requires C, 73·5; H, 10·2 per cent.)

The p-*Nitrophenylhydrazone* crystallised from alcohol in small, reddish flakes, m.p. 154–55°. (Found: N, 7·9. $C_{30}H_{45}O_5N_3$ requires N, 8·0 per cent.)

7:8-*Diacetoxy*-2-*methyl*-3-*hexadecyl-chromone* crystallised from alcohol in white, flat needles, m.p. 92–93°. (Yield = 65 per cent.) It was soluble in the usual organic solvents, insoluble in alkali solution and gave straw-yellow colour with concentrated sulphuric acid. Its alkaline hydrolysis gave exclusively 4-stearyl-pyrogallol. (Found: C, 72·2; H, 8·8. $C_{30}H_{44}O_6$ requires C, 72·0; H, 8·8 per cent.)

6-*Bromo*-4-*Stearyl-pyrogallol* crystallised from alcohol in white needles, m.p. 86–87° (depressed to 65° by the original ketone). (Found: Br, 17·2. $C_{24}H_{39}O_4Br$ requires Br, 17·0 per cent.)

The bromo-derivative was not affected by hot alkali solution, and could not be further brominated.

6-*Nitro*-4-*Stearyl-pyrogallol* crystallised from alcohol in white, flat needles, m.p. 95–96°. (Found: N, 3·1. $C_{24}H_{39}O_6N$ requires N, 3·2 per cent.)

4-*Octadecyl-pyrogallol* crystallised from alcohol in brown needles, m.p. 114–15°, and was soluble in the usual organic solvents, but sparingly so in hexane. Its alcoholic solution did not give any coloration with ferric chloride. (Found: C, 76·3; H, 11·2. $C_{24}H_{42}O_3$ requires C, 76·2; H, 11·1 per cent.)

4-*Palmityl-pyrogallol* crystallised from alcohol in white, lustrous needles, m.p. 84–85°. Soluble in the usual organic solvents, its alcoholic solution gave violet coloration with ferric chloride. (Yield = 65 per cent.) (Found: C, 72·4; H, 9·9. $C_{22}H_{36}O_4$ requires C, 72·5; H, 9·9 per cent.)

The p-*Nitrophynelhydrazone* crystallised from alcohol in reddish, flat needles, m.p. 171–72°. (Found: N, 8·4. $C_{28}H_{41}O_5N_3$ requires N, 8·4 per cent.)

7:8-*Diacetoxy*-2-*methyl*-3-*tetradecyl-chromone* crystallised from hexane in lustrous flakes, m.p. 104–05°. It dissolved in concentrated sulphuric acid with a fine, yellow colour. (Yield = 70 per cent.) (Found: C, 71·0; H, 8·8. $C_{28}H_{40}O_6$ requires C, 71·2; H, 8·5 per cent.)

The alkaline hydrolysis of the chromone gave entirely 4-palmityl-pyrogallol.

6-*Bromo*-4-*palmityl-pyrogallol* crystallised from alcohol in white, lustrous needles, m.p. 87–88°. (Found: Br, 18·1. $C_{22}H_{34}O_4Br$ requires Br, 18·0 per cent.)

6-*Nitro*-4-*palmityl-pyrogallol* crystallised from alcohol in white, lustrous flakes, m.p. 92–93°. (Found: N, 3·3. $C_{22}H_{35}O_6N$ requires N, 3·4 per cent.)

4-*Hexadecylpyrogallol* crystallised from hexane in white needles, m.p. 115–16°. Its alcoholic solution did not give any colour with ferric chloride. (Found: C, 75·3; H, 10·8. $C_{22}H_{38}O_3$ requires C, 75·4; H, 10·9 per cent.)

4-*Lauryl-pyrogallol* was obtained in 65 per cent. yield and crystallised from hexane in white, lustrous needles, m.p. 74-75°. Its alcoholic solution gave violet coloration with ferric chloride. (Found: C, 70·0; H, 9·0. $C_{18}H_{28}O_4$ requires C, 70·1; H, 9·1 per cent.)

The p-*Nitrophenylhydrazone* crystallised from alcohol in reddish needles, m.p. 182–83°. (Found: N, 9·4. $C_{24}H_{33}O_4N_3$ requires N, 9·5 per cent.)

6-*Bromo*-4-*lauryl-pyrogallol* crystallised from alcohol in small yellowish flakes, m.p. 80–81°. (Found: Br, 20·5. $C_{18}H_{27}O_4Br$ requires Br, 20·7 per cent.)

The bromo derivative was unaffected by hot alkali solution and could not be further brominated.

4-*Dodecylpyrogallol* crystallised from hexane in small, lustrous needles, m.p. 170–71°. Easily soluble in most of the organic solvents, its alcoholic solution did not give any coloration with ferric chloride. (Found: C, 73·3; H, 10·3; $C_{14}H_{30}O_3$ requires C, 73·5; H, 10·2 per cent.)

We take this opportunity to thank Prof. R. N. Bhagwat and Rev. Father G. Palacios, S.J., for their kind interest and provision of facilities for the work.

Summary

Resorcinol and pyrogallol have been condensed with stearic, palmitic and lauric acids to obtain the dihydroxy and trihydroxy ketones. Chromones have been prepared from them, and it is observed that the resulting γ-pyrones gave only the orignial ketones on alkaline hydrolysis, and not

a trace of the *o*-hydroxy-carboxylic acids. As most of these ketones were prepared for the first time, their bromination, nitration and reduction were studied. The last reaction gave resorcinols and pyrogallols containing octadecyl, hexadecyl and dodecyl-groups in the 4-position.

REFERENCES

1. Desai and Waravdekar, *Proc. Ind. Acad. Sci.* (A), 1940, **12**, 507.
2. Heilbron and co-workers, *J.*, 1933, 1263 ; 1934, 1311, 1581 ; 1936, 295.
3. Klarmann, *Jour. Amer. Chem. Soc.*, 1926, **48**, 2358.

HETEROCYCLIC COMPOUNDS

Part XIII. Abnormal Alkaline Hydrolysis of Some 4-Isopropyl-1 : 2-α-Naphthapyrones

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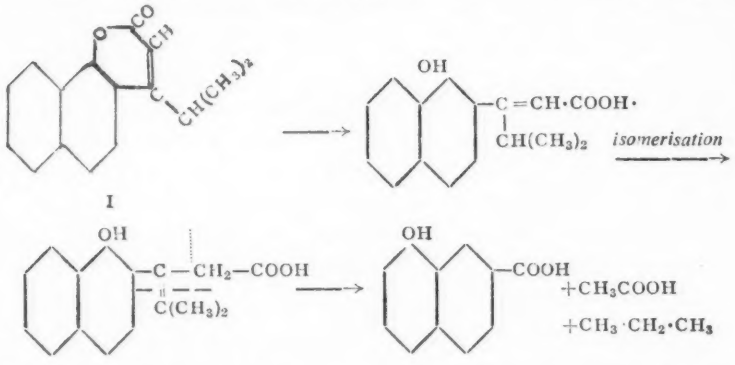
Received October 31, 1940

By the acetylation of 2-isobutyryl-1-naphthol according to Kostanecki's method, we obtained a compound having the composition $C_{14}H_{16}O_2$. In the absence of a $COCH_2R$ group ortho to the hydroxyl, this method cannot give a chromone, and therefore, we have assumed the coumarin structure for it. However, when we hydrolysed it by heating with 5 per cent. caustic soda, only 1-hydroxy-2-naphthoic acid was obtained. The formation of an *o*-hydroxy-carboxylic acid[1] by this method has been usually accepted as the criterion of the chromone structure, but never that of the coumarin which is supposed to give usually *o*-hydroxy-cinnamic acid[2] or, in rare cases, *o*-hydroxy-ketone as recently shown by Sethna and Shah.[3] However, if the hydrolysis of the coumarin (I) takes the course indicated as follows, the formation of *o*-hydroxy-carboxylic acid can be easily explained.

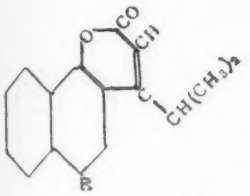


I

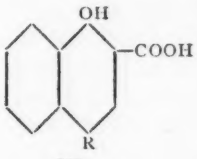
2-Isobutyryl-1-naphthol is not the intermediate product during the hydrolysis of this coumarin, as this hydroxy-ketone can be recovered unchanged under identical conditions. 4-Bromo-2-isobutyryl-1-naphthol, and 4-acetyl-2-isobutyryl-1-naphthol gave 4-isopropyl-6-bromo-1 : 2-α-naphthapyrone (II, R = Br) and 4-isopropyl-6-acetyl-1 : 2-α-naphthapyrone (II,

R = $CoCH_3$), which underwent alkaline hydrolysis to 4-bromo-1-hydroxy-2-naphthoic (III, R = Br) and 4-acetyl-1-hydroxy-2-naphthoic acids (III, R = $CoCH_3$) respectively.

These observations serve to emphasise the fact that the results of the alkaline hydrolysis cannot be always relied upon as an unequivocal method for the identification of coumarins and chromones. However, we wish to collect more examples of such abnormal hydrolysis by extending these observations to 4-isopropylbenzo-α-pyrone, as well as its substitution products which are easily obtainable by the Pechmann condensation of isobutyryl-acetic ester and its C-alkyl derivatives with the phenols.



II



III

Before concluding, we wish to make a passing reference to a new method which we have evolved for the diagnosis of the coumarins and chromones. When bromine in glacial acetic acid solution is added to the coumarin or the chromone dissolved in the same solvent, the former invariably gives the bromo-substitution derivative while the latter gives the di-per-bromide from which the original chromone can be regenerated by the action of aqueous sulphurous acid. However, we wish to make this a subject of future communication.

Experimental

2-Isobutyryl-1-naphthol was prepared by the modification of the method of Goldzweig and Kaiser.[4] To a solution of anhydrous zinc chloride (20 g.) in isobutryic acid (20 g.), α-naphthol (20 g.) was added and the mixture was poured into water after heating to boiling on the sand-bath for two hours. The black, semi-solid mass was purified through 5 per cent. alkali when a considerable quantity of neutral products was removed. The acidic material was exhaustively extracted with hexane which dissolved 2-isobutyryl-1-naphthol, leaving impurities of a dinaphthol type insoluble. Finally the crystallisation from alcohol gave pale-yellow, square plates, m.p. 87–88° (literature gives 77°). Mixed m.p. with an authentic specimen of 2-butyryl-1-naphthol was 65°. (Yield = 25 per cent.) (Found: C, 78·4; H, 6·6. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·5 per cent.)

Its alcoholic solution gave dark green colouration with ferric chloride.

Kostanecki Reaction with 2-*Isobutyryl*-1-*naphthol and Formation of* 4-*Isopropyl*-1 : 2-α-*naphthapyrone*.—A mixture of 2-isobutyryl-1-naphthol (10 g.), anhydrous sodium acetate (20 g.) and acetic anhydride (50 c.c.) was heated at 175–80° for 12 hours, and poured into water. The solid after being triturated with 5 per cent. alkali, crystallised from hexane in thick white plates, m.p. 105°. (Yield = 90 per cent.) (Found: C, 80·4; H, 6·1, $C_{16}H_{14}O_2$ requires C, 80·7; H, 5·9 per cent.)

It was soluble in alcohol, acetone, acetic acid, and benzene, and dissolved in concentrated sulphuric acid without any colour or fluorescence.

Hydrolysis of the Coumarin to 1-*Hydroxy*-2-*naphthoic Acid*.—A suspension of the coumarin (1 g.) in 5 per cent. NaOH (50 c.c.) was heated on sand-bath under reflux for four hours when a clear solution was obtained. The cooled filtered solution gave, on acidification with concentrated HCl, a solid which was purified through sodium bicarbonate solution, and crystallised from alcohol in needles, m.p. 195°, undepressed by admixture with an authentic specimen of 1-hydroxy-2-naphthoic acid.

4-*Bromo*-2-*isobutyryl*-1-*naphthol*.—When Bromine (2·5 c.c.) was gradually added to the solution of 2-isobutyryl-1-naphthol (10 g.) in glacial acetic acid (150 c.c.), copious fumes of HBr were evolved. The mixture was exposed to sunlight for two hours and kept overnight before pouring into water. The solid that slowly separated out crystallised from alcohol in square plates, m.p. 71° (depressed to 34° by 4-bromo-2-butyryl-1-naphthol). (Found: Br, 27·0. $C_{14}H_{13}O_2$ Br, requires Br, 27·3 per cent.)

Kostanecki Reaction with 4-*Bromo*-2-*isobutyryl*-1-*naphthol and Formation of* 6-*Bromo*-4-*isopropyl*-1 : 2-α-*naphthapyrone*.—The reaction was carried out at 175–80° for 12 hours using 4-bromo-2-isobutyric acid (4 g.), sodium acetate (8 g.) and acetic anhydride (20 c.c.) and the coumarin isolated as usual. It crystallised from alcohol in small, colourless plates m.p. 98°. (Yield = 3·5 g.) (Found: Br, 25·1; $C_{16}H_{13}O_2$ Br requires Br, 25·2 per cent.)

Hydrolysis of the Coumarin to 4-*Bromo*-1-*hydroxy*-2-*naphthoic Acid*.—The hydrolysis was carried out as usual. The acid, purified through sodium bicarbonate solution crystallised from alcohol in white needles, m.p. 244-45°, and was identified as 4-bromo-1-hydroxy-2-naphthoic acid by comparison with an authentic specimen.

4-*Acetyl*-2-*isobutyryl*-1-*naphthol*.—Acetyl chloride (9 g.) was gradually added with constant shaking to a mixture of powdered anhydrous zinc

chloride (20 g.) 2-isobutyryl-1-naphthol (20 g.) and nitrobenzene (120 c.c.). After 30 hours, the mixture was worked up as usual, and the solid that separated out after the removal of nitrobenzene in steam crystallised from alcohol in pale-yellow needles, m.p. 80° (depressed to 60° by 4-acetyl-2-butyryl-1-naphthol). The substance is soluble in dilute (2–3 per cent.) alkali, but forms an insoluble sodium salt in concentrated solutions (5–10 per cent.). Its alcoholic solution gave a violet colouration with ferric chloride. (Found: C, 74·7; H, 6·4. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3 per cent.)

Kostanecki Reaction with 4-*Acetyl*-2-*isobutyryl*-1-*naphthol and Formation of* 6-*Acetyl*-4-*isopropyl*-1 : 2-α-*naphthapyrone.*—The mixture of the naphthol (3 g.), sodium acetate (6 g.) and acetic anhydride (25 c.c.) was heated at 175–80° for 12 hours. The product isolated as usual crystallised from hexane in small plates, m.p. 85°. (Found: C, 76·8; H, 5·8. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·7 per cent.)

The coumarin was hydrolysed as usual, and the acid which after purification melted at 215°, was identified as 4-acetyl-1-hydroxy-2-naphthoic acid by comparison with an authentic specimen. This acid gave, on decarboxylation, 4-acetyl-1-naphthol, m.p. 200°, already described by Akram and Desai.[5]

Summary

4-Isopropyl-1 : 2-α-naphthapyrone is hydrolysed by dilute alkali to 1-hydroxy-2-naphthoic acid. It is further observed that 6-bromo- and 6-acetyl-4-isopropyl-1 : 2-α-naphthapyrones are also hydrolysed to 4-bromo- and 4-acetyl-1-hydroxy-2-naphthoic acids. As the hydrolysis of the coumarins to *o*-hydroxy carboxylic acids is unusual, these cases provide interesting exceptions to the usual behaviour.

REFERENCES

1. Baker, *J.*, 1925, 2349.
2. Canter and Robertson, *Ibid.*, 1931, 1875.
3. Sethna and Shah, *J, Ind. Chem. Soc.*, 1940, **17**, 211.
4. Goldzweig and Kaiser, *J. Pr. Chem.*, (2), **43**, 97.
5. Akram and Desai, *Proc. Ind. Acad. Sci.*, (A), 1940, **11**, 149.

AN ELEMENTARY THEORY OF THE CORONAS OF WATER DROPLETS

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1. Introduction

As is well known, a bright source of light seen through a thin cloud of water droplets appears overlaid by a bright disc of light and coloured rings concentrically surrounding it. The phenomenon may be observed in the laboratory with clouds artificially produced by sudden expansion of moist air contained in a large glass vessel and viewing a bright source of light through the same. In such observations, it is noticed that when the water droplets in the cloud are sufficiently small, the central disc of the corona instead of being white, appears strongly coloured. The succession of colour in the outer rings is also found to vary with the size of the water droplets. Moreover when the source of light is monochromatic, the configuration of the outer rings and their relative intensities vary remarkably with the size of the drops (Mitra, 1928). These facts indicate that the usual elementary theory of the coronas in which the water droplets are regarded as opaque spherical obstacles diffracting light is inadequate. Mecke (1920) has attempted a treatment of the case in which the actual transparency of the droplets is taken into account. His approach to the problem is based partly on the principles of geometrical optics and partly on the elementary theory of diffraction and is therefore not a strictly coherent treatment based on the wave principles alone.

In the present paper, a theory of coronas will be presented in which, instead of assuming the droplets to be perfectly opaque, they will be considered as perfectly transparent, in other words, allow the incident waves to pass right through producing only a phase retardation corresponding to the difference in the refractive index between the liquid and the surrounding medium. The smaller this difference is, the more perfectly should such a treatment represent the actual facts of the case. The merit of the treatment proposed is that it enables us to understand the physical reason why the diffraction effects produced by a transparent drop differ so little from those due to opaque spheres, and also indicate when these differences must be expected to become sensible.

2. *General Theory*

In the ordinary treatment of diffraction of light by water droplets, the droplets are assumed to be equivalent to opaque discs of the same

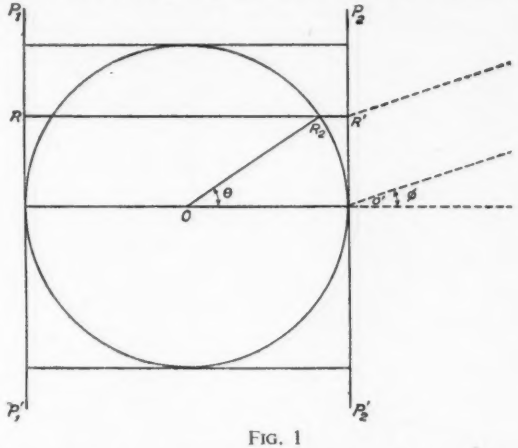

FIG. 1

diameter. By the application of Babinet's principle which states that if a large opening is covered by a great number of opaque discs and illuminated,

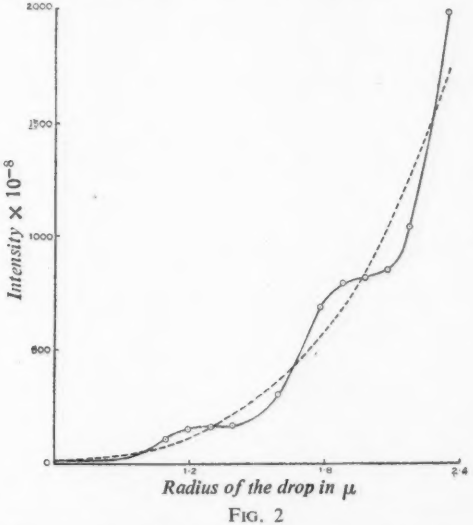

FIG. 2

then the resulting illumination will be just the same, but in exactly opposite phase, if the opaque discs should become transparent and the transparent

interspaces opaque, the problem is altered from one of diffraction by an opaque disc to one of diffraction by a circular opening. The relevant theory is well known. The displacement in any direction making an angle ϕ with the direction of the beam, when r is the distance of any element of the circle from its centre (O′) and α the angle between the line joining this element to the centre and the radius (a) of the opening in the horizontal plane at O′, is given in the usual notation by

$$\mathrm{E}\cos\frac{2\pi}{\lambda}\,[ct'+r\cos\alpha\sin\phi]\,rdrd\alpha.$$

The positive sign is explained by the fact that the optical path from R′ is less than that from O′. In our present considerations, we take into account the path retardation of $\{2a+2(\mu-1)a\cos\theta\}$ which occurs in the passage of the wave through the drop. This retardation is partially set off by the difference in path mentioned above. The expression for the displacement is accordingly

$$\mathrm{E}\cos\frac{2\pi}{\lambda}\,[ct-2(\mu-1)a\cos\theta+r\cos\alpha\sin\phi]\,rdrd\alpha$$

where $ct=ct'-2a$.

At a distance d, the displacement due to the wavefront which has traversed the drop is

$$\int_0^{a/2}\int_0^{2\pi}\frac{\mathrm{E}}{\lambda d}\sin\frac{2\pi}{\lambda}\,[ct-2(\mu-1)a\cos\theta+r\cos\alpha\sin\phi]\,rdrd\alpha.$$

Substituting $r=a\sin\theta$, the expression for the displacement is transformed into

$$\int_0^{\pi/2}\int_0^{2\pi}\frac{\mathrm{E}a^2}{\lambda d}\sin\frac{2\pi}{\lambda}\,[ct-2(\mu-1)a\cos\theta+a\sin\theta\cos\alpha\sin\phi]$$
$$\sin\theta\cos\theta\,d\theta\,d\alpha.$$

Substituting,

$$\chi=\frac{2\pi}{\lambda}ct$$

$$n_1=\frac{4\pi(\mu-1)a}{\lambda}$$

$$n_2=\frac{2\pi a\sin\beta}{\lambda}$$

and simplifying, the displacement becomes

$$\text{Sin } \chi \frac{Ea^2}{\lambda d} \int_0^{\pi/2} \int_0^{2\pi} \cos (n_2 \cos \alpha \sin \theta) \cos (n_1 \cos \theta) \sin \theta \cos \theta d\theta \, d\alpha$$

$$- \cos \chi \frac{Ea^2}{\lambda d} \int_0^{\pi/2} \int_0^{2\pi} \cos (n_2 \cos \alpha \sin \theta) \sin (n_1 \cos \theta) \sin \theta \cos \theta \, d\theta \, d\alpha \tag{1}$$

Now the effect of the original undisturbed wavefront over the area covered by the drop is obtained by substituting $\mu = 1$ in the above expression, in which case, the second term vanishes and the first reduces to

$$\text{Sin } \chi \frac{Ea^2}{\lambda d} \int_0^{\pi/2} \int_0^{2\pi} \cos (n_2 \cos \alpha \sin \theta) \sin \theta \cos \theta \, d\theta \, d\alpha$$

$$= \frac{2 \pi a^2 E}{\lambda d} \cdot \frac{J_1 (n_2)}{n_2} \cdot \sin \chi \tag{2}$$

The diffracted wave due to the wavefront which has traversed the drop is obtained by subtracting (2) from (1) since in the limit, when $\mu \to 1$, the diffracted wave should vanish. Integration with respect to α gives the result for the displacement:

$$\text{Sin } \chi \frac{2 \pi a^2 E}{\lambda d} \int_0^{\pi/2} J_0 (n_2 \sin \theta) \cos (n_1 \cos \theta) \sin \theta \cos \theta \, d\theta$$

$$- \cos \chi \frac{2 \pi a^2 E}{\lambda d} \int_0^{\pi/2} J_0 (n_2 \sin \theta) \sin (n_1 \cos \theta) \sin \theta \cos \theta \, d\theta$$

$$- \frac{2 \pi a^2 E}{\lambda d} \cdot \frac{J_1 (n_2)}{n_2} \cdot \sin \chi.$$

3. *The Forward Scattering*

In the forward direction, $\beta = 0$; $n_2 = 0$; and the integrals may be evaluated completely. We have,

$$I_F = \frac{E^2}{d^2} \cdot \frac{4 \pi^2 a^4}{\lambda^2} \left[\left(\frac{\cos n_1 - 1 + n_1 \sin n_1}{{n_1}^2} - \tfrac{1}{2} \right)^2 + \left(\frac{\sin n_1 - n_1 \cos n_1}{{n_1}^2} \right)^2 \right]$$

The intensity of the light diffracted in the forward direction by particles of radius increasing from $0 \cdot 6 \mu$ to $2 \cdot 4 \mu$ was calculated with the following assumptions:

$$r = 1$$
$$E = 1$$
$$\lambda = 4358 \text{ Å}$$
$$\mu = 1 \cdot 33$$

The intensities according to (1) the opaque disc formula and (2) the diffraction formula here derived are tabulated. For particles with radius below $0{\cdot}6\,\mu$, an elementary theory of this kind can hardly be applicable even as an approximation.

TABLE I

Radius in μ	Intensity ($\times 10^{-8}$) according to the		Radius in μ	Intensity ($\times 10^{-8}$) according to the	
	Ordinary Formula	Modified Formula		Ordinary Formula	Modified Formula
0·6	6·7	10·2	1·4	199	164
0·7	12·5	10·8	1·6	341	305
0·8	21·3	12·7	1·8	546	685
0·9	34·1	24·3	2·0	832	808
1·0	52	56·3	2·2	1220	1030
1·2	108	148	2·4	1725	1970

4. *Discussion*

A curve has been drawn showing the intensities according to the two formulæ indicated in Table I. It is easily seen that the effect of considering the droplet as transparent is to introduce in the intensity expression a correction term which induces a periodic fluctuation and the magnitude of the correction is relatively more important for the smaller sizes. With increasing size the correction becomes relatively less important, showing that for large sizes the effect of the transparency of the droplet is negligible and the curve tends to approximate to that given by the usual formula for an opaque disc. It will be noticed that the curve of the intensities shows a series of oscillations following each other at intervals of $0{\cdot}7\mu$, corresponding to a path-difference of one wavelength in the passage of light through the drop as compared with the exterior. Qualitatively, this appears to be in accord with observational results since, as Mecke has shown, the colours in the central part of the corona change, with gradually increasing size of the drop, in the spectral order and in the range of radii between $1\,\mu$ and $2{\cdot}4\,\mu$, traverse the cycle from violet to purple twice over, indicating that a complete cycle corresponds to an increase in the radius of the drop by about $0{\cdot}7\,\mu$. The experimental data available are, however, inadequate to decide between the merits of the new formula derived here and that of Mecke. The question whether any elementary treatment is capable of satisfactorily

explaining the vivid colours observed in the central disc of the corona also needs examination. It seems possible that the phenomenon is the result of dielectric resonance and fully explicable only on the basis of the electromagnetic theory. This question, as also the configuration of the outer rings in the corona will be considered in a later communication.

The author desires to express his thanks to Prof. Sir C. V. Raman, F.R.S., for his kind encouragement and keen interest in the investigation.

5. *Summary*

In the usual theory of coronas the water droplets are considered as opaque discs. In the present paper, they are treated as perfectly transparent spheres in passing through which the wavefronts undergo a phase retardation. An expression is derived for the intensity of the diffracted radiation which is completely evaluated for the forward direction. A comparison with the usual formula for an opaque disc shows a difference which oscillates with increasing size of the drop and ultimately becomes very small in magnitude. The colours observed in the central disc of the corona for small sizes are thus qualitatively explained.

REFERENCES

1. Mecke .. *Ann. d. Phys.*, 1920, **61**, 471.
2. ——— .. *Ibid.*, 1920, **62**, 623.
3. Mitra .. *Ind. J. Phy.*, 1928, **3**, 175.

THE LANTHANUM NITRATE TEST FOR ACETATE IN INORGANIC QUALITATIVE ANALYSIS

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Damour[1] found that when lanthanum salts are treated with iodine and ammonia in the presence of acetic acid or acetates under suitable conditions, a dark blue precipitate or a blue solution is obtained. Though this reaction has been known for a long time, it is only during recent years that Krüger and Tschirch have adopted the reaction for the detection of the acetate ion. In a series of papers[2–9] these authors have shown that the test is more delicate than any previously described for acetate, it being as sensitive as the starch test for iodine and quite as satisfactory for the detection of acetate and acetic acid in organic and inorganic material.

The test has been shown to be applicable in the presence of a large number of inorganic acid radicles.[7,10] Nitrates, chlorides, bromides and iodides do not affect the sensitiveness of the test even when present in excess but they weaken the intensity of the blue colour. Sulphates, however, interfere in relatively small amounts, though they do not precipitate the lanthanum. Other anions such as the phosphate, fluoride, tartrate, oxalate (which precipitate the lanthanum) and the cations which are precipitated by ammonia, interfere. It has also been found that potassium iodide, or a large excess of acetate itself, tends to transform the blue colour into a yellowish brown.[3] The test is very sensitive and can detect as small a quantity as 0·1 to 0·05 mg. of acetic acid, the concentration limit being 1 in 2,000 of water.[10, 11]

Krüger and Tschirch have suggested the elimination of sulphate and phosphate[7] with barium nitrate, the test being carried out with the filtrate. Large amounts of nitrate and chloride can be removed by making use of the fact that sodium acetate is considerably more soluble than sodium nitrate or chloride in absolute alcohol.[8] Oxalic acid is removed by oxidation with bromine water. Separation from tartaric acid is effected by the distillation of acetic acid.[7] It has also been suggested that distillation of the easily volatile acetic acid is serviceable for the preparation of a suitable solution for the test.[8]

In the course of the qualitative analysis of mixtures of inorganic substances including the organic radicles, acetate, oxalate and tartrate, the need for a satisfactory test for the acetate ion has been frequently felt. Several of the available tests are unsatisfactory for one reason or another. The frequently suggested test with ferric chloride is not satisfactory as pointed out by Curtman and Harris,[12] while the cacodyl oxide test cannot be recommended for general use on account of the extremely poisonous character of the product. Further, it is well known that success with the ethyl acetate test which is most commonly used, is largely dependant on personal factors. The difficulties of this test are also enhanced by the presence in the mixtures of acid radicles which evolve gases with dilute or concentrated sulphuric acid. The expedient of pouring the solution, after esterification with concentrated sulphuric acid, into water is not always satisfactory. The use of amyl alcohol[13,14] in the place of ethyl alcohol is also unsatisfactory for the same reasons. It is apparent, therefore, that a visual test would be far superior to the olefactory ones. Tests based on crystal formation with sodium uranyl formate or cholesterol are in use in micro-chemical work but they cannot be recommended for routine analysis. Colour tests based on (*a*) the reduction of acetic acid to the aldehyde with magnesium and dilute hydrochloric acid[15] or (*b*) the dry distillation of the calcium salt with calcium formate,[16] and the testing of the aldehyde with sodium nitroprusside, and (*c*) the production of acetone by the dry distillation of calcium acetate and the testing of the vapours with alkaline *o*-nitrophenol or *o*-nitrobenzaldehyde[17,18] are all unsuitable for mixtures of inorganic substances met with in routine analysis.

Though the lanthanum nitrate colour test has been included among tests for acetate by McAlpine and Soule[19] as well as by Engelder and Dunkelberger,[14] it appears that no attempt has so far been made to adapt this test for routine analysis of mixtures of inorganic substances including the acetate, oxalate and tartrate radicles. Lanthanum nitrate (Merck's "Pure") is not much more expensive than silver nitrate and the authors of this paper, therefore, felt it desirable to study the application of this reaction in routine analysis.

Experimental

Preparation of Reagents—

(1) *Lanthanum Nitrate Solution.*—5·0 g. of a sample of the "pure" salt supplied by the firm of Merck was dissolved in 100 ml. of water.

(2) *Iodine Solution.*—Krüger and Tschirch,[2,4] and Engelder and Dunkelberger (*loc. cit*) used an alcoholic solution of iodine to avoid

possible interference from potassium iodide. On the other hand, Feigl[11] apparently uses an aqueous solution containing potassium iodide.

The iodine solution employed in the present investigation was prepared by diluting a 0·1 N aqueous solution of iodine containing potassium iodide, prepared for volumetric analysis, with water to yield a 0·02 N solution. There was no noticeable interference in the test from the potassium iodide.

(3) *Ammonia Solution.*—The bench dilute ammonia solution (2 N) was diluted with water to yield 1·0 N solution.

Distillation of Acetic Acid from the Mixture—

The procedures recommended for the elimination of the interfering radicles by previous workers are elaborate and slow. The sodium carbonate extract which is commonly used for the identification of acid radicles is not satisfactory for while it removes most of the interfering metals, it leaves the interfering acid radicles in solution. Distillation, as suggested by Krüger and Tschirch (*loc. cit.*), of the acetic acid in the mixture with dilute sulphuric acid and absorption of the vapours in water was, therefore, considered to be the most suitable method for the preparation of the solution.

Slightly different procedures, as described below, were adopted according to the presence or absence in the mixture of sulphites and thiosulphates as shown by preliminary tests. The distillation was ordinarily carried out in a test-tube provided with a cork and a delivery tube but when the volume was large or bumping anticipated, a small distilling flask provided with a suitable adapter with an elongated tip was used. In both cases the vapours were received under a small amount of water placed in a test-tube.

(*a*) *In the Absence of Sulphites and Thiosulphates.*—The mixture (2–3 g.) was treated with an excess of dilute sulphuric acid (4 N) and after allowing sufficient time for any effervescence present to cease, the mixture distilled for 5–10 milutes.

(*b*) *In the Presence of Sulphites and Thiosulphates.*—The mixture (2–3 g.) was acidified with a large excess of dilute sulphuric acid and treated gradually with an excess of a saturated solution of potassium permanganate to oxidise the sulphur dioxide. The mixture was then distilled for 5–10 minutes as before.

Detection of Acetate—

The aqueous distillate was cooled and treated successively with 1 c.c. of lanthanum nitrate solution, a slight excess of the iodine solution and a few drops of dilute ammonia. If no blue colour developed within a minute,

the solution was gradually heated to boiling. When an acetate was present in the mixture, a dark blue colour was frequently obtained in the cold itself and without failure on gradually heating to boiling. On setting aside the boiled liquid, a deep blue gelatinous precipitate separated out in most cases when an acetate was present. If no acetate was present, only a greyish gelatinous precipitate was obtained on boiling.

Results

A large number of mixtures containing several combinations of the common acid radicles and including especially those that are likely to interfere, were examined. When no permanganate was used for the oxidation of sulphur dioxide, sulphites and thiosulphates interfered on account of the formation of the interfering sulphate ion during the test. The presence in the distillate of moderate amounts of free chlorine or bromine, oxides of nitrogen from nitrites or hydrogen sulphide from sulphides, did not interfere with the test, provided enough iodine solution was added to leave a small excess of free iodine, and was followed by sufficient dilute ammonia. In the presence of sulphites and thiosulphates in the mixture, addition of an excess of a saturated solution of potassium permanganate to the acidified mixture was found to be quite effective in preventing the liberation of sulphur dioxide. Using this modification it was found that no interference occurred with any of the common acid radicles and the results were quite satisfactory for acetate. When mixtures which did not contain the acetate radicle were examined, uniformly negative results were obtained. It was also found during this investigation that it was advisable to prescribe distillation for 5–10 minutes in all cases since in a few cases shorter periods were found to be insufficient.

Conclusion

The lanthanum nitrate test for the acetate ion has been examined for use in the routine analysis of mixtures of inorganic substances including the acetate, oxalate and tartrate radicles. A distillation method for the preparation of the test solution and a modification of this procedure in the presence of sulphites and thiosulphates are described. The results obtained are quite satisfactory and the test is recommended for general use.

The authors wish to thank Professor T. R. Seshadri for his interest in the work.

REFERENCES

1. Damour .. *Acad. Sci. Paris*, 1857, **43**, 976.
2. Krüger and Tschirch .. *Ber.*, 1929, **62B**, 2776.
3. ———— .. *Ibid.*, 1930, **62B**, 826.
4. ———— .. *Mikrochemie*, 1930, **2**, 337 ; (*Cf. Chem. Abs.*, 1931, **25**, 894).
5. ———— .. *Ibid.*, 1930, **8**, 218.
6. ———— .. *Pharm. Zentralhalle*, 1930, **71**, 145 ; (*Cf. Chem. Abs.*, 1930, **24**, 2083).
7. ———— .. *Pharm. Acta. Helv.*, 1930, **5**, 25 ; (*Cf. Chem. Abs.*, 1930, **24**, 5002).
8. Tschirch .. *Oesterr. Chem. Ztg.*, 1931, **34**, 38 ; (*Cf. Chem. Abs.*, 1931, **25**, 2665).
9. Krüger and Tschirch .. *Dyestuffs*, 1931, **32**, 91 ; (*Cf. Chem. Abs.*, 1932, **26**, 298).
10. Feigl-Mathews .. " Spot tests " (1937), p. 299.
11. Erdös .. *Chem. Abs.*, 1931, **25**, 2390.
12. Curtman and Harris .. *J. Am. Chem. Soc.*, 1917, **39**, 1315.
13. Rosenthaler .. *Pharm. Zentralhalle*, 1933, **74**, 288 ; (*Cf. Chem. Abs.*, 1933, **27**, 3893).
14. Engelder and Dunkelberger .. " Semi-micro Qualitative Analysis," 1936, p. 244.
15. Doeuvre .. *Bull. Soc. Chim.*, 1933, **53**, 1532 ; (*Cf. Chem. Abs.*, 1934, **28**, 3338).
16. Sanchez .. *Chem. Abs.*, 1936, **30**, 4432.
17. Feigl, *et al.* .. *Mikrochemie*, 1935, **17**, 165 ; (*Cf. Chem. Abs.*, 1935, **29**, 5385).
18. Rosenthaler .. *Ibid.*, 1937, **23**, 194 ; (*cf. Chem. Abs.*, 1938, 32, 1609).
19. McAlpine and Soule .. " Qualitative Chemical Analysis," 1933, p. 452.

CHEMICAL INVESTIGATION OF INDIAN LICHENS

Part III. The Isolation of Montagnetol, A New Phenolic Compound from *Roccella montagnei*

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In a previous communication[1] it was stated that the lichen *Roccella montagnei* differs markedly in chemical composition, depending upon the season. Erythrin, erythritol, lecanoric acid, roccellic acid and orcinol were found to be the main components along with isolichenin. It was further recorded that orcinol which was obtained from the ether and acetone extracts was contaminated with a tenacious impurity which rendered purification extremely difficult and wasteful. This was obviously due to the close similarity that existed between the contaminating impurity and orcinol, particularly in regard to their solubility in ordinary solvents. However, as the result of repeated attempts using a combination of solvents, it has now become possible to separate the crude orcinol mixture into two components, (1) orcinol and (2) montagnetol, a new crystalline compound. The details of the procedure are described in the experimental part.

The name 'Montagnetol' has been given to the new compound with a view to indicate its occurrence in *Roccella montagnei* and its nature as a phenol. It resembles orcinol in regard to its ready solubility in water, alcohol and acetone, and in its colour reaction with ferric chloride and bleaching powder, but it differs from orcinol in its high melting point (154–56°) its sparing solubility in ether, benzene and chloroform, and in not giving the homofluorescein reaction. It seems to have the molecular formula $C_{13}H_{20}O_7$. Montagnetol has been all along accompanying orcinol in the several samples examined during the years 1938–39, the quantity present being small. In a number of samples collected during August, September and October 1940 it has been found to be the major component, the other substances being orcinol, roccellic acid and erythritol. These samples contained neither erythrin nor lecanoric acid in any detectable quantity.

Experimental

Separation of montagnetol and orcinol.—The crude orcinol mixture was dissolved in the minimum quantity of acetone and after filtering off any undissolved impurity, the solution was diluted with an equal volume of ether. This mixture was then treated with chloroform or benzene until

turbidity was produced and allowed to stand overnight. A colourless crystalline solid (montagnetol) in the form of lens-shaped crystals separated out. Very often a semi-solid mass was obtained and it turned crystalline after further repetition of the treatment or allowing to stand for a considerable length of time. The solid was separated and the mother liquor slowly concentrated, further quantities of the substance being collected at different stages if possible. It was again recrystallised using the mixture of solvents, acetone, ether and benzene or chloroform. Final concentration of the mother liquors yielded pure orcinol melting at 57–58° and it was found to be identical with an authentic sample of the monohydrate.

The separation of the crude mixture could also be effected in the following manner though it involved some loss of material and could not be adopted with larger quantities. A small quantity of it was placed on a porous tile and a few drops of water slowly added. Orcinol dissolved readily and the solution was absorbed by the tile almost immediately leaving montagnetol almost pure and colourless. The sample thus obtained could be easily crystallised from a mixture of acetone, ether and benzene. By extracting the porous tile with hot water, orcinol could be recovered, but it was always contaminated with small amounts of montagnetol.

The new compound montagnetol is easily soluble in water, alcohol and acetone and insoluble in benzene, chloroform and solvent spirit. Even though it is extracted along with orcinol from the lichen by means of ether, the purified compound is only sparingly soluble in this solvent. An aqueous solution of the substance gave a bright violet colour with ferric chloride and an orange red colour with bleaching powder. It is neutral to litmus and does not evolve carbon dioxide with sodium bicarbonate. When treated with chloroform and alkali it does not give the greenish-yellow fluorescence characteristic of orcinol (Found : C, 53·9; H, 6·4 ; molecular wt. by Rast's method 314 ; $C_{13}H_{20}O_7$ requires C, 54·2 ; H, 6·9% and molecular weight 288).

The following is a description of a third representative extraction relating to the samples of the lichen collected during the months of August, September and October, 1940. They contained montagnetol, roccellic acid, erythritol and orcinol.

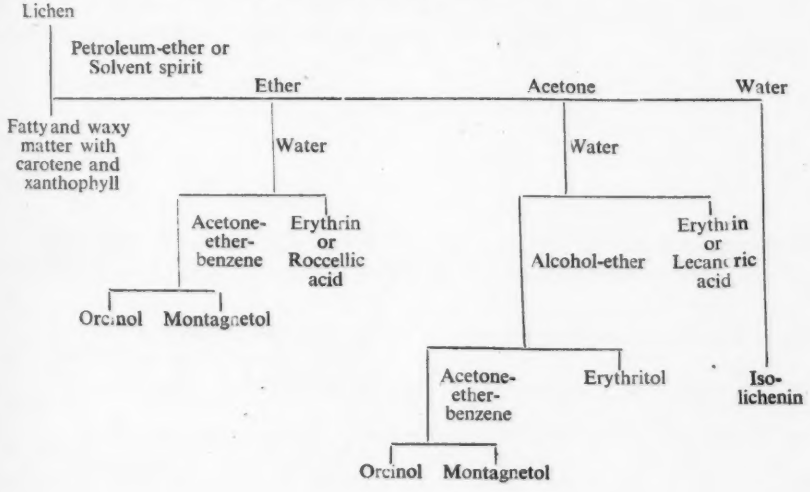
Extraction with solvent spirits for 24 hours yielded fatty and waxy matter along with some carotenoid pigments as found before. On subsequent extraction with ether for 48 hours a crystalline solid separated in the receiver the supernatant liquid being deeply coloured. The clear solution (*c*) was carefully poured out, the solid washed with small quantities of ether and the washings added to the original solution (*c*). The solid residue was then

crystallised from a mixture of acetone, ether and benzene and was found to be identical with a pure sample of montagnetol. From the coloured solution (*c*) ether was distilled off and thereby a green-coloured sticky residue was obtained. It was treated with water which dissolved a portion. From the water-insoluble residue pure roccellic acid was obtained after one recrystallisation from alcohol. On evaporating the aqueous solution a mixture of orcinol and montagnetol was left in the residue and was separated as already described.

The lichen sample was next extracted with acetone for 48 hours. On distilling off the solvent from the extract a reddish-brown solid was left and it was almost completely soluble in water yielding a red aqueous solution. The water-insoluble residue was very small. It was green in colour and did not give any crystalline product on purification. The aqueous solution was evaporated to dryness on a water-bath and the reddish-brown crystalline residue washed repeatedly with small quantities of a mixture of alcohol and ether (1 : 1). A colourless crystalline solid melting at 120–21° was thus obtained and was identified as erythritol. The alcohol-ether solution on evaporation yielded a mixture of orcinol and montagnetol.

The yields of the pure crystalline compounds obtained from this sample of the lichen were montagnetol 1·8%, erythritol 1·6%, roccellic acid 0·8% and orcinol 0·1%.

In view of the discovery of montagnetol, the following table has been drawn up in order to summarise comprehensively the processes adopted for the separation of the components of the lichen.



Summary

The isolation of a new phenolic compound, 'Montagnetol' from the lichen *Roccella montagnei* and its properties are described. The details of the extraction of a sample of the lichen which contained it as the major component are given.

LITERATURE REFERENCE

1. Subba Rao and Seshadri .. *Proc. Ind. Acad. Sci.* (A), 1940, 5, 466.

ON THE EXISTENCE OF A METRIC FOR PATH-SPACES ADMITTING THE LORENTZ GROUP*

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I. This note discusses the existence of a metric for the most general path-spaces admitting only the Lorentz group of the special theory of relativity.

I shall use the notation of Kosambi[1] throughout this note with the exception that X, Y, Z are used in place of the corresponding curly (Gothic) letters in his paper.

The equations, under discussion, have already been given by Kosambi[1] in the following form :—

$$\ddot{x}^i - p^i \, \mathrm{H}(\mathrm{X}, \mathrm{Y}, \mathrm{Z}) + \dot{x}^i \, \mathrm{J}(\mathrm{X}, \mathrm{Y}, \mathrm{Z}) = 0, \qquad (1)$$

where H, J are arbitrary.

By a metric for the space defined by (1), we shall mean the integrand $f(\mathrm{X}, \mathrm{Y}, \mathrm{Z})$ of any regular problem of the calculus of variations whose extremals are defined by the equations (1). For the existence of such a metric, a set of necessary and sufficient conditions are derived from the condition that the equations of variation of (1) be self-adjoint.[2]

These conditions are :

$$\begin{aligned} &(a) \quad J_{;\,i;\,r} P^r_j - f_{;\,r;\,j} P^r_i = 0, \\ &(b) \quad \mathcal{D} f_{;\,i;\,j} = 0, \qquad (2) \\ &(c) \quad |f_{;\,i;\,j}| \neq 0, \text{ where} \end{aligned}$$

$\mathcal{D}$ is the Kosambian derivate, P^i_j is his mixed curvature tensor of the path-space and semicolon denotes differentiation with respect to $\dot{x}$.

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* I express my thanks to Prof. D. D. Kosambi for his kind guidance and helpful suggestions throughout the course of this investigation.

[1] D. D. Kosambi, " Path-equations admitting the Lorentz group," *Lond. Math. Soc.*, 1940, 15, 86-91.

[2] D. D. Kosambi, *Quarterly Jour. Maths.*, 1935, **6**, 1–12 (See also the paper of D. R. Davis referred to therein).

The mixed tensor $P^i{}_j$ for the space defined by (1) takes the following form :

$$P^i{}_j = A\delta^i_j + B\dot{x}^i \dot{x}_j + C\dot{x}^i p_j + D\dot{x}_j p^i + Ep^i p_j \; ; \qquad (3)$$

where,

$$A \equiv ZHJ_2 + \tfrac{1}{2} X HJ_3 - YJJ_2 - \tfrac{1}{2} ZJJ_3 + ZJ_1 + \tfrac{1}{2} YJ_3 + H + \tfrac{1}{4} J^2,$$

$$B \equiv 2 ZHJ_{22} + X HJ_{23} - JJ_2 - 2 YJJ_{22} - ZJJ_{23} - H_2 + 2ZJ_{12} + YJ_{23} - \tfrac{1}{2} J_3 - ZJ_2H_2 + YJ^2{}_2 - \tfrac{1}{2} XH_2J_3 + \tfrac{1}{2} ZJ_2J_3,$$

$$C \equiv HJ_2 + ZHJ_{23} + \tfrac{1}{2} XHJ_{33} - YJJ_{23} - \tfrac{1}{2} ZJJ_{33} - \tfrac{1}{2} H_3 + ZJ_{13} + \tfrac{1}{2} YJ_{33} - 2 J_1 - \tfrac{1}{2} ZJ_2H_3 + \tfrac{1}{2} YJ_2J_3 - \tfrac{1}{4} X J_3H_3 + \tfrac{1}{4} ZJ^2{}_3,$$

$$D \equiv - 2ZHH_{22} - X HH_{23} + HJ_2 + 2YJH_{22} + ZJH_{23} - 2 ZH_{12} + \tfrac{1}{2} H_3 - YH_{23} + ZH^2{}_2 - YJ_2H_2 + \tfrac{1}{2} X H_2H_3 - \tfrac{1}{2} ZJ_2H_3,$$

$$E \equiv - HH_2 - ZHH_{23} - \tfrac{1}{2} XHH_{33} + \tfrac{1}{2} HJ_3 + YJH_{23} + \tfrac{1}{2} ZJH_{33} - ZH_{13} - \tfrac{1}{2} YH_{33} + 2 H_1 + \tfrac{1}{2} ZH_2H_3 - \tfrac{1}{2} YH_2J_3 + \tfrac{1}{4} X H^2{}_3 - \tfrac{1}{4} ZJ_3H_3 - \tfrac{1}{2} JH_3.$$

Here the suffixes 1, 2, 3 denote differentiation with respect to X, Y, Z respectively.

We have, accordingly

$$f_{;\,i;\,j} = 2\, g_{ij} f_2 + 4\, \dot{x}_i\, x_j f_{22} + p_i\, p_j f_{33} + 2\,(\dot{x}_i\, p_j + \dot{x}_j\, p_i)\, f_{23} \qquad (4)$$

The condition (2, *a*) for the given values of $\rho_j{}^i$ (3) and $f_{;\,i;\,j}$ (4) leads to a linear partial differential equation of the second order for the function f :

$$2\,(C - D) f_2 + 4\,(CY + EZ)\, f_{22} + 2\,(CZ + EX - BY - DZ) f_{23} - (BZ + DX) f_{33} = 0 \qquad (5, a)$$

The condition (2, *b*) gives the following set of equations :

$$- Jf_2 + 2\, Zf_{12} + 2\,(HZ - YJ) f_{22} + (Y + XH - ZJ) f_{23} = 0, \qquad (5, b)$$

$$2\, H_3 f_2 + (4\, H + 2\, ZH_3 - 2\, YJ_2) f_{23} + (XH_3 - J - ZJ_3) f_{33} + 2Zf_{331} + 2\,(ZH - YJ) f_{233} + (Y + XH - ZJ) f_{333} = 0, \qquad (5, c)$$

$$- J_2 f_2 + (2\, ZH_2 - 2YJ_2 - 3J) f_{22} + (1 + XH_2 - ZJ_2) f_{23} + 2\, Zf_{221} + (Y + XH - ZJ) f_{223} + 2\,(ZH - YJ) f_{222} = 0, \qquad (6, a)$$

$$(2H_2 - J_3) f_2 + (4\, H + 2\, ZH_3 - 2\, YJ_3) f_{22} + (-4\, J + 2\, ZH_2 - 2\, YJ_2 + XH_3 - ZJ_3) f_{23} + (1 + XH_2 - ZJ_2) f_{33} + 4\, Zf_{123} + (2\, Y + 2\, XH - 2\, ZJ) f_{233} + 4\,(ZH - YJ) f_{223} = 0 \qquad (6, b)$$

Out of these five equations (5, *a*, *b*, *c*), 6 (*a*, *b*) we shall select those which are independent and of the lowest possible order. By ordinary calculation we find that (6, *a*) is obtained by differentiating (5, *b*) with respect to Y and, therefore, can be ignored. Again, differentiating (5, *b*) with respect to Z and subtracting twice of the differential equation from (6, *b*) we get a new equation of the second order :

$$(2\,H_2 + J_3)\,f_2 - 4\,f_{21} - 2\,(ZH_3 - YJ_3)\,f_{22} + (-XH_3 + ZJ_3 + 2\,ZH_2 - 2\,YJ_2)\,f_{23} + (1 + XH_2 - ZJ_2)\,f_{23} = 0 \qquad (5, d)$$

So the system of partial differential equations for the unknown function f are (5, *a b*, *c*, *d*).

As an aid to integration we find two more differential equations got directly from Euler's equation :

$$\frac{d}{dt} f_{;i} - f_{;i} = 0 \qquad (7)$$

$$-Jf_2 + 2\,Zf_{12} + 2\,(HZ - YJ)f_{22} + (Y + XH - ZJ)f_{23} = 0, \qquad (7, a)$$

$$-2\,f_1 + 2\,H\,f_2 + 2\,Z\,f_{13} + 2\,(ZH - YJ)\,f_{23} + (Y + XH - ZJ)\,f_{33} = 0 \,(7, b)$$

Equation (7, *a*) is the same as the equation (5, *b*) and (5, *c*) follows from (7, *b*) by differentiating it with respect to Z. But nothing is gained by taking (7, *b*) in place of any of the others because it is known that our set (5, *a–d*) would be necessary and sufficient for the existence of a metric. This seems a contradiction at first, which is easily explained by the well-known fact that one integrand of a variational problem can only be determined to an additive perfect differential. The solution of (7, *b*) can differ atmost by such an additional term from the set (5).

We know that our system of equations (5) admit a solution, for if we take $f = A\,(X)\,Z + B\,(X)$ all the equations are satisfied. But this is a trivial case which does not satisfy the condition (2, *c*). In order to get the most general non-trivial solution we must, in general, restrict the arbitrary functions H, J. Although our system is not of the linear first order partial differential equation type, we can nevertheless discuss the necessary conditions for the existence of a non-trivial metric by reduction to a linear first order system.

We can eliminate f_{33} from equations (5, *a*) and (5, *d*). This gives a new equation :

$$\{2\,(C-D)\,(1+XH_2-ZJ_2)+(BZ+DX)\,(2\,H_2+J_3)\}$$
$$f_2-4\,(BZ+DX)\,f_{21}$$
$$+\{4\,(CY+EZ)\,(1+XH_2-ZJ_2)-2\,(ZH_3-YJ_3)\,(BZ+DX)\}f_{22}$$
$$+\{2\,(CZ+EX-BY-DZ)\,(1+XH_2-ZJ_2)$$
$$+(BZ+DX)\,(ZJ_3+2\,ZH_2-XH_3-2\,YJ_2)\}f_{23}$$
$$=0 \qquad (8)$$

Now the equations (5, *b*) and (8) can be considered linear equations of the first order in $f_2=\phi$ (say). Writing these equations in the following forms :

$$\nabla_1\phi \equiv \alpha_1\phi+\beta_1\phi_1+\gamma_1\phi_2+\delta_1\phi_3=0, \qquad (5,b)$$

$$\nabla_2\phi \equiv \alpha_2\phi+\beta_2\phi_2+\gamma_2\phi_2+\delta_2\phi_3=0, \qquad (8)$$

We calculate the Poisson's brackets[3] and get one more equation

$$\nabla_3\phi \equiv (\nabla_1\nabla_2-\nabla_2\nabla_1)\phi \equiv \alpha_3\phi+\beta_3\phi_1+\gamma_3\phi_2+\delta_3\phi_3=0. \qquad (9)$$

If $\alpha_3, \beta_3, \delta_3, \gamma_3$ all vanish, the system $\nabla_1\phi=\nabla_2\phi=0$ is integrable ; if $\beta_3=\gamma_3=\delta_3=0$, $\alpha_3\neq 0$, only trivial solution exists. In the general case we repeat the process once more and get,

$$\nabla_4\phi \equiv (\nabla_1\nabla_3-\nabla_3\nabla_1)\,\phi \equiv \alpha_4\phi+\beta_4\phi_1+\gamma_4\phi_2+\delta_4\phi_3=0, \qquad (10)$$

$$\nabla_5\phi \equiv (\nabla_2\nabla_3-\nabla_3\nabla_2)\,\phi \equiv \alpha_5\phi+\beta_5\phi_1+\gamma_5\phi_2+\delta\,\phi_3=0. \qquad (11)$$

Therefore, we get two necessary conditions for the existence of a non-trivial metric.

$$(a)\quad \begin{vmatrix} \alpha_1 & \beta_1 & \gamma_1 & \delta_1 \\ \alpha_2 & \beta_2 & \gamma_2 & \delta_2 \\ \alpha_3 & \beta_3 & \gamma_3 & \delta_3 \\ \alpha_4 & \beta_4 & \gamma_4 & \delta_4 \end{vmatrix} = 0,$$

$$(b)\quad \begin{vmatrix} \alpha_4 & \beta_1 & \gamma_1 & \delta_1 \\ \alpha_2 & \beta_2 & \gamma_2 & \delta_2 \\ \alpha_3 & \beta_3 & \gamma_3 & \delta_3 \\ \alpha_5 & \beta_5 & \gamma_5 & \delta_5 \end{vmatrix} = 0. \qquad (12)$$

The process is not to be continued further because it is known that if (12) be satisfied, all further operators will be linearly dependent on ∇_1, ∇_2, ∇_3.

Conditions (12) are justified, because we could not with f a non-trivial solution get as many as four linearly independent operators $\nabla_i\phi=0$ of the present type.

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[3] T. Levi-Civita, *The Absolute Differential Calculus*, Ch. III.

If the equations (12) are satisfied, we can always integrate—in theory, though the actual process in practice need not be simple—for f_2, and have determined f, but for an additive arbitrary function of (X, Z). The additive function can be determined to within a perfect differential by substitution in the second order equation (5, *c*). It would have been pleasant to find the general existence conditions and solution explicitly, but this can be done only by transferring the equations to a less cumbersome set, hence is postponed for some future note.

It is to be noticed that there are just two Euler equations, and four in the system (5, *a–d*); yet each set is supposed to lead to the metric. The fact is that the equations (5, *b*) is common to both. Of the remaining three in the set (5), (5, *c*) and (5, *d*) can be eliminated from Euler equations as follows :

Differentiating (7, *b*) with respect to Z we get (5, *c*). Again differentiating (7, *a*) with respect to Z and (7, *b*) with respect to Y and subtracting the results so obtained we get equation (5, *d*). So, there only remains only one extra equation in (5), namely, (5, *a*) which cannot be deduced from the Euler equations. This is to be explained by well-known theoretical considerations.[2] Because equations (2) determine $f_{;\,i;\,j}$, f is undetermined in the great case only to within an additive term of type A (X) Z + B (X). This accounts for the difference in the two sets of equations. The best procedure would be to find an integral, if one exists, of our set $\nabla_i \phi = 0$, and substitute in the Euler equations to determine the additional terms.

II. There does not exist, in general, a non-trivial solution for the most general set of H, J. If the space admits a metric, such that any non-trivial function $\psi(f)$ is also a metric, the conditions (2) reduce to the following form :[4]

$$\mathcal{D} f = 0, \; ; f_{ji} = 0, \text{ along with } |J_{;\,i;\,j}| \neq 0, \tag{13}$$

where | represents covariant differentiation in Kosambian sense.

Because the invariant metric (in Kosambi's terminology) f does not contain the parameter t, the above condition reduce to

$$\epsilon^r f_{;\,r} = 0 \; ; f_{j\,i} = 0, \tag{13, *a*, *b*}$$

where $\epsilon^r = \alpha^r - \frac{1}{2}\alpha^r{}_{;i}\,\dot{x}^{i}$ [5]

$$\alpha^r = -p^r \mathrm{H} + \dot{x}^r \mathrm{J}$$

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[4] D. D. Kosambi, "Modern differential geometries," *Ind. Jour. Phys.*, 1932.

[5] ————, " Parallelism and Path-Spaces," *Math. Zeitschrift*, 1933, **37**.

The two conditions lead to the following system of differential equations for f:

$$\nabla_1 f \equiv 2f_1 + (ZH_3 - YJ_3) f_2 + (\tfrac{1}{2} XH_3 - \tfrac{1}{2} J - \tfrac{1}{2} ZJ_3) f_3 = 0 \quad (14, a)$$

$$\nabla_2 f \equiv (2ZH_2 - J - 2YJ_2) f_2 + (1 + XH_2 - ZJ_2) f_3 = 0 \quad (14, b)$$

$$\nabla_3 f \equiv (-2ZH + YJ + 2YZH_2 + Z^2H_3 - 2Y^2J_2 - YZJ_3) f_2$$
$$+ (-XH + XYH_2 + \tfrac{1}{2} XZH_3 - YZJ_2 - \tfrac{1}{2} Z^2J_3 + \tfrac{1}{2} ZJ) f_3 = 0 \quad (14, c)$$

From this set of equations we infer that the following conditions must be satisfied for the existence of a metric :

(i) the second order determinant formed out of the coefficients of f_2 and f_3 in (14, b), (14, c) must be zero, *i.e.*,

$$-XJH + (2Z^2 - 2XY) HJ_2 + 2YZH_2 - 2Y^2J_2 + (2XY - Z^2) JH_2$$
$$- YZJJ_2 - 2ZH + YJ + Z^2H_3 - YZJ_3 + (Z^3 - XYZ)(J_3H_2 - J_2H_3) \quad (15)$$
$$+ \tfrac{1}{2} XZJH_3 + \tfrac{1}{2} ZJ^2 - \tfrac{1}{2} Z^2JJ_3 = 0.$$

This condition being satisfied, we proceed to find out a second condition for the existence of a metric.

From the compatibility conditions of (13) we know that

$$P_j^i f_{;i} = 0^5$$

$$\text{Now, } P_j^i f_{;i} \equiv (2A\dot{x}_j + 2BY\dot{x}_j + 2CYp_j + 2DZ\dot{x}_j + 2EZp_j) f_2 \quad (16)$$
$$+ (Ap_j + BZ\dot{x}_j + CZp_j + DX\dot{x}_j + EXp_j) f_3 = 0.$$

From (16), equating the coefficients of $\dot{x}_j$, p_j we get two equations:

$$(2A + 2BY + 3DZ) f_2 + (BZ + DX) f_3 = 0 \quad (16, a)$$

$$(2CY + 2EZ) f_2 + (A + CZ + EX) f_3 = 0, \quad (16, b)$$

A, B, C, D, E as in formula (3).

The second condition that a metric should exist is that of the four equations, namely (14, b, c) and (16, a, b) each pair must be dependent.

If we take the paths as those with the most general Lorentz invariant symmetric affine connection, we have :

$$H = \frac{aY}{X} + \frac{bZ^2}{X^2}, \; J = \frac{2cZ}{X}, \quad (17)$$

a, b, c are functions of X only. In this case the condition (15) is satisfied. For the second condition we form the determinant out of the coefficients of equations (14, b), (16, a), and get after taking the common factor.

$$\begin{vmatrix} a-c & a+1 \\ \left(\frac{bc}{X}-\frac{c^2}{X}+2c'-\frac{2c}{X}+\frac{2b}{X}\right. & \left(-\frac{c}{X}-\frac{ac}{X}-2a'+\frac{a}{X}\right. \\ \left.-2a'+\frac{2a}{X}+\frac{a^2}{X}+\frac{ab}{X}\right) & \left.+\frac{b}{X}+\frac{a^2}{X}+\frac{ab}{X}\right) \end{vmatrix} = 0 \qquad (18)$$

$$\text{or, } X\left(\frac{a'}{1+a}-\frac{c'}{1+c}\right)=a+b-c \qquad (18, a)$$

The vanishing of the other determinants formed by taking any other pair gives the same result.

The equation (14, c) is identically satisfied for the values (17) specified to H, J.

If a, b, c are constant (18, a) gives $a+b=c$ the condition for the existence of a metric.*

Although it is learnt that (2, a, b) are always satisfied when $\mathcal{D}f=f_{1,i}=0$, it is not without interest to derive the set (5) from (14, a–c) in the following manner.

(1) Multiply (14, a) by Z, (14, b) by Y, add them. We get the equation

$$2Zf_1+2(ZH-YJ)f_2+(XH+Y-ZJ)f_3=0 \qquad (19)$$

Differentiating (19) with respect to Y and substracting from the result (14, b) we get (5, b).

(2) Multiply (14, a) by 2 and differentiating with respect to Y and subtracting the result from the differentiated result of (14, b) with respect to Z we get (5, d).

(3) Differentiate (19) with respect to Z and subtract from the result twice of (14, a) we get (7, b) which differentiated with respect to Z gives (5, c).

The equation (5, a) cannot easily be deduced from (14) in the above manner. But if we proceed in a way parallel to the theory we can deduce it from the invariant form of equations (13).

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* I am obliged to Prof. D. D. Kosambi for communicating to me these conditions (18, a). He had obtained them by a direct method, but has not yet seen fit to publish his results. His general condition for non-degeneracy $(a+1)(c+1)\neq 0$ has not been obtained here.

We know that if $\mathcal{D}f = 0, f_{1\,i} = 0$, then

$$P_j^i\, f_{;\,i} = 0^5$$

Therefore differentiating (16) with respect to $\dot{x}^r$ we get,

$$\begin{aligned}
&\{2\,Ag_{rj} + 2\dot{x}_j(2\,A_2\dot{x}_r + A_3p_r) + 2\,BYg_{rj} + 4\,B\dot{x}_j\dot{x}_r \\
&+ 2\,Y\dot{x}_j(2\,B_2\dot{x}_r + B_3p_r) + 4\,Cp_j\dot{x}_r + 2\,Yp_j(2\,C_2\dot{x}_r + C_3p_r) \\
&+ 2\,D\,p_r\dot{x}_j + 2\,DZg_{rj} + 2\,Z\dot{x}_j(2\,D_2\dot{x}_r + D_3p_r) \\
&+ 2\,Ep_rp_j + 2\,Zp_j(2\,E_2\dot{x}_r + E_3p_r)\}f_2 + \\
&+ (2\,A\dot{x}_j + 2\,BY\dot{x}_j + 2\,CYp_j + 2\,ZD\dot{x}_j + 2\,ZEp_j) \\
&\qquad (2f_{22}\dot{x}_r + f_{23}p_r) + \\
&+ \{p_j(2\,A_2\dot{x}_r + A_3p_r) + BZg_{rj} + Bp_r\dot{x}_j + Z\dot{x}(2\,B_2\dot{x}_r + B_3p_r) \\
&+ Cp_rp_j + Zp_j(2\,C_2\dot{x}_r + C_3p_r) + DXg_{rj} + X\dot{x}_j(2\,D_2\dot{x}_r + D_3p_r) \qquad (20) \\
&+ Xp_j(2\,E_2\dot{x}_r + E_3p_r)\}f_3 \\
&+ (Ap_j + BZ\dot{x}_j + CZp_j + DX\dot{x}_j + EXp_j) \\
&\qquad (2f_{23}\dot{x}_r + f_{33}p_r) = 0
\end{aligned}$$

Again, $\frac{\partial}{\partial \dot{x}^j}(P_r^i f_{,i})$ can be found by interchanging j and r in equation (20)

$$\begin{aligned}
&\therefore \frac{\partial}{\partial \dot{x}^r}(P_j^i f_{;\,r}) - \frac{\partial}{\partial \dot{x}^j}(P_r^i f_{;\,i}) \\
&= (\dot{x}_j p_r - \dot{x}_r p_j)\{(2\,(D - C)f_2 - 4\,(CY + EZ)f_{22} \\
&\qquad + (2BY + 2\,DZ - 2CZ - 2EX)f_{23} \\
&\qquad + (BZ + DX)f_{33}\} \\
&+ (\dot{x}_j p_r - \dot{x}_r p_j)\{(2A_3 + 2YB_3 - 2C - 4YC_2 + 2ZD_3 + 4ZE_2)f_2 \\
&\qquad + (-2\,A_2 + B + ZB_3 - 2ZC_2 + XD_3 \\
&\qquad - 2\,X\,E_2)\,f_3\}
\end{aligned}$$

i.e., 0 = the left-hand side of equation (5, *a*) + 3 $R_{jr}^i f_{;\,i}$

But, $R_{jr}^i\, f_{;\,i} = 0^5$ which follows from $f_{1i} = 0$.

Thus (5, *a*) is deduced from (13).

SUBSTITUTION IN POLYCYCLIC SYSTEMS*

Part II. The Nitroderivatives of Fluoryl 9-Trimethylammonium Compounds

By S. V. Anantakrishnan and V. Pasupati

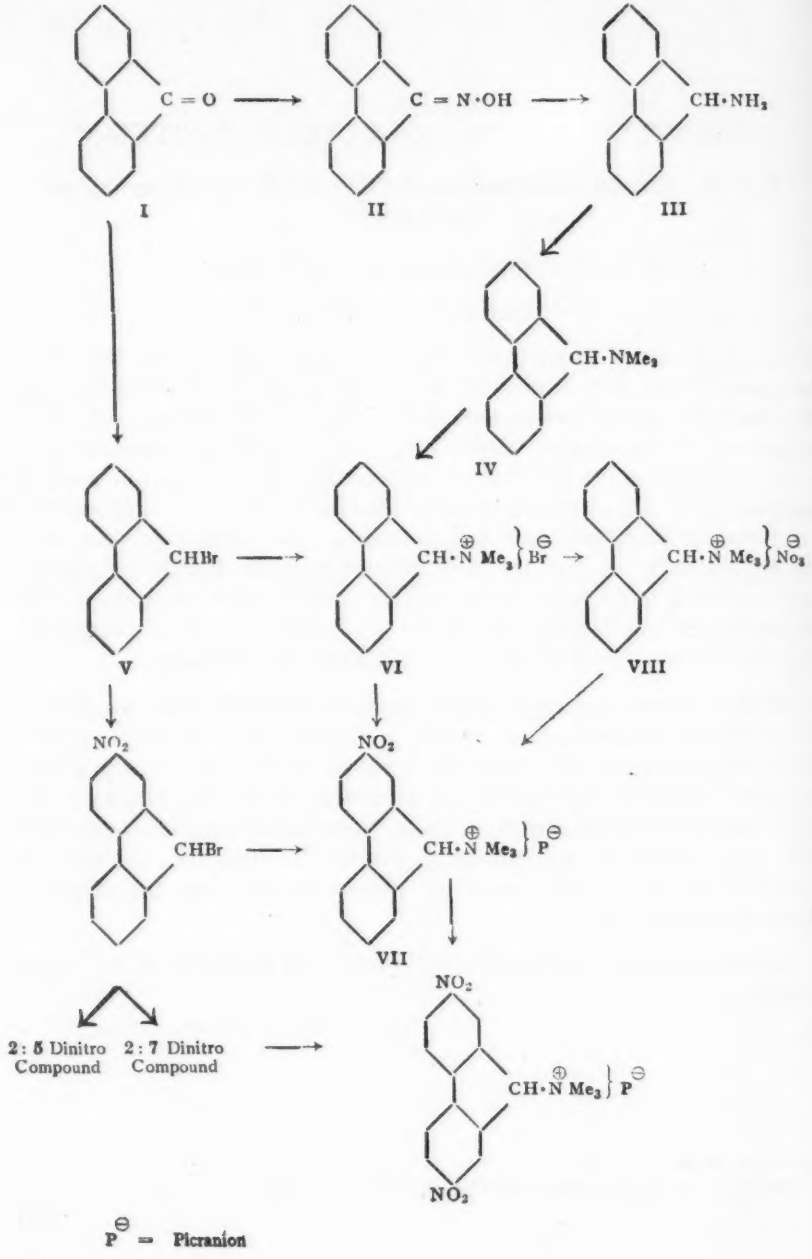
(Received October 21, 1940)

In the nitrations of 9-substituted fluorene compounds, it has been found that generally the introduction of substituent groups in the 9-position does not affect the general orientation in the nucleus even though the relative proportions of the isomers might vary. In the case of 9-bromofluorene it was noticed that the introduction of a second nitro group was predominantly in the 7-position while a small amount of the 2 : 5 compound and a number of other products were obtained, the dinitro product being obtained as easily as with the unsubstituted fluorene though the nitration conditions had to be kept under greater control; with an average room temperature in our laboratories of 30° C., a rigid control of temperature below 15° C. was found necessary to minimise side reactions.

With a closed system of mobile electrons involving the two benzene nuclei and the cyclopentadiene system, a 9-substituent may be expected to disturb substitution in other positions especially if a strong electron attracting group (class – I of Ingold's classification) is in that position. The present paper deals with studies involving quaternary ammonium compounds which were needed by the authors in another investigation. A report on the studies on 9-nitro and 9-carbonyl derivatives will form the subject of a later communication.

The experimental investigation was carried out according to the following scheme:—

* For Part I see Anantakrishnan and Hughes, *J.C.S.*, 1935, 1607.



$P^{\ominus}$ = Picranion

Schmidt and Stutzel[6] reported the production of two compounds by reducing II, both being considered stereoisomeric forms of 9-aminofluorene. Kuhn and Jacob[5] also report several forms. Ingold and Wilson,[4] however, find that only one form of III is obtained along with some acetyl derivative. We have carried out the reduction several times and in all cases obtained only one form of 9-aminofluorene confirming the observations of Ingold and Wilson (*loc. cit.*).

For the conversion of III into its dimethyl derivative (IV), Stevens[8] uses formaldehyde as the methylating agent carrying out the reaction in a pressure bottle at 130°. We find that without recourse to high temperature or pressure, this methylation could be smoothly carried out with dimethyl sulphate and excess alkali, the reaction taking a shorter time.

For the preparation of the quaternary ammonium compound, the method involving 9-bromofluorene was found more convenient and has been adopted in the experiments.

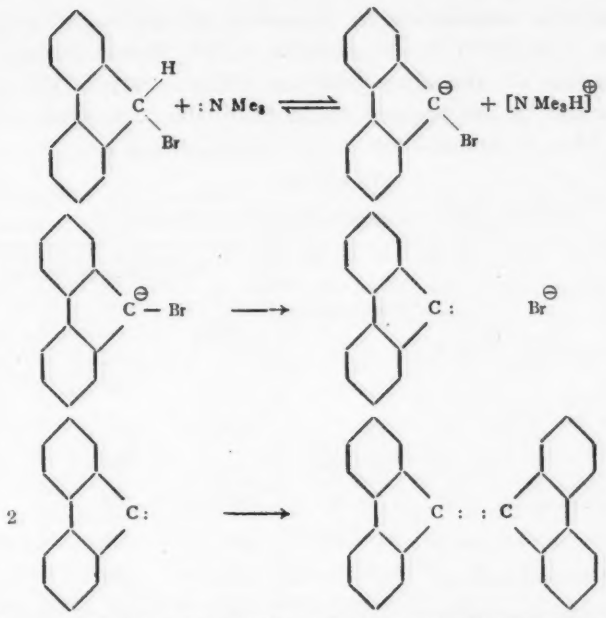
The mono-nitro 'Onium compound could be easily prepared either by nitrating the unsubstituted salt or by reacting 2-nitro 9-bromofluorene with trimethylamine in acetonitrile. Here also the entrance of the nitro group in the 2-position shows that a 9-substituent does not materially affect the orientation. It must be borne in mind that in the nitration of the salt it is only the cation that is concerned and the ease of nitration is independent of the nature of the anion.

The preparation of the corresponding dinitro compounds by direct nitration of the salt under mild conditions, however, gave very unsatisfactory results. The isomeric 2:5 and 2:7 dinitrofluoryl 9-trimethyl ammonium compounds could be obtained by dinitration of 9-bromofluorene and controlled reaction of these with trimethylamine. Boiling of the salt with fuming nitric acid appears to be necessary for the introduction of a second nitro group which goes predominantly in the 7-position.

Here we have a striking illustration of the difference between the corresponding sulphonium and ammonium compounds. Under conditions which yield directly the dinitrosulphonium compound (Hughes and Kuriyan[1]), the fluoryl 9-trimethyl ammonium salts give only a mononitro product. From *a priori* considerations it can be shown that the quaternary ammonium "pole" exerts a greater deactivating influence than the corresponding sulphonium "pole" and it is also well known that the mechanism of elimination is more complex in the case of sulphonium compounds. With a powerful electron attracting group, the deactivating influence is only to be

expected. A substituent in the side chain usually exerts a comparatively feeble influence on the reactivity of the nucleus but the 9-position in fluorene has to be considered differently. The electronic structure of fluorene and the fluoryl radical visualises the cyclopentadiene ring as part of the system of mobile electrons and consequently one has to expect transmission of group influences when these are sufficiently powerful as in the present case. Consequently both benzene nuclei are deactivated and slow nitration is the result. With the introduction of the first nitro group, this deactivating influence is greatly augmented and further nitration becomes very difficult, the conditions approximating to that of trinitration of 2:7 dinitro fluorene. Here again, is noticed the similarity between diphenyl and fluorene. In both classes polynitro compounds are obtained only by indirect means.

The present series of compounds also illustrate the converse of this influence, substituents in other positions affecting reactivity in the 9-position. The facile transmission of electromeric and inductive effects by the cyclopentadiene system is noticed here also. As is well known, the nitro group (–I–T) promotes reactivity towards nucleophilic reagents and retards reactivity towards electrophilic reagents. In benzene this influence is most noticeable in the ortho and para-positions by electromeric relay. In the present studies this same effect is noticed with 9-substituents in fluorene. Taking substituted 9-bromo-fluorenes, the two reactions that may be envisaged involve either elimination of bromine as an anion or that of hydrogen as a cation. In one case we have the disruption of a C–Br linkage and in the other a C–H linkage. When a substituted 9-bromo compound reacts with trimethylamine, two reactions are therefore possible the formation of an 'Onium compound which will be considered in a later paper and the formation of a bis-fluorenylidine:



The evidence for this ionic *cum* free radical mechanism is at present purely circumstantial and it is hoped at a later stage to adduce more definite experimental proof. The series of colour changes that is invariably noticed in this reaction together with the necessity for an excess of the base render this scheme plausible. It must be pointed out here that the introduction of solvents in which ionisation may not be expected, considerably slows down the reaction giving the halogen-free compound. The introduction of a nitro group in the nucleus facilitates the egress of the proton and the bis-fluorinylidene compound is readily obtained. A second nitro group in the nucleus makes this reaction almost quantitative (Table I). It is

TABLE I

Compound	% Halogen-free compound formed with NMe_3
9-Bromofluorene	0
2-Nitro-9-Bromofluorene	10–20
2:7-Dinitro-9-Bromofluorene	80
2:5-Dinitro-9-Bromofluorene	99

significant that the stabilisation of a negative charge on the ter-covalent 9-carbon atom is facilitated by the presence of nitro groups in the nucleus.[1]

The influence of the nitro group is felt not only in the chemical behaviour but also on the physical properties of the compounds studied as may be seen from an examination of the table (Table II).

TABLE II

Melting points of some derivatives of fluorene

	Unsubstituted	Substituents in Nucleus		
		2-Nitro	2:7-Dinitro	2:5-Dinitro
Fluorene	114·5°	156–57	295–300	207
Fluorenone	85	221	292	241
9-Bromofluorene	103–104·5	145	260	199
Fluoryl 9-trimethyl-ammonium bromide	189–90	198–200	225	..
Fluoryl 9-trimethyl-ammonium picrate	170–75	226	235–36	209–10
Fluoryl 9-dimethyl sulphonium bromide	133	130–35	230	..
Fluoryl 9-dimethyl sulphonium picrate	149–50	185	255–60	..

In all the series the 2:7 compounds, like the para derivatives in benzene, the 2:6 or 1:5 derivatives in naphthalene and 4, 4′ derivatives of diphenyl exhibit the highest melting point. Any systematic correlation between structure and melting point in the present series has, however, to meet the limitations set by the chemical behaviour of the compounds. In a number of cases of the substituted compounds, especially those in the last three columns, the " melting points " really represent the temperature of decomposition of the compounds as it has often been found that the rate of heating appeared to modify the melting point. The values given refer to results obtained under comparable rates of heating. We can then readily understand the very close range in the 'Onium series. It is interesting to note in this connection that corresponding sulphonium compounds also present a similar anomalous position. In both cases, we have the " electron sink " nitro groups reinforcing the 'Onium pole so as to facilitate the easy removal of the proton which represents the first step in the elimination reaction.

Experimental

Oxidation of fluorene.—A modification of the method of Schmidt and Wagner[7] was adopted. The reaction was allowed to proceed at or below

100° C. Higher temperatures were found to give more of by-products. The vigorous reaction in the early stages had to be controlled by cooling. The yield (90%) was better than that of Huntress and Cliff,[2] m.p. 85° C.

The oxime [m.p. 195° C. (yellow needles from dilute alcohol)] was prepared by the usual methods.

Reduction of Fluorenone Oxime.—9-Aminofluorene was obtained by a modification of earlier methods[4] using diluted (92%) acetic acid to minimise the formation of the acetyl derivative. The hydrochloride was crystallised from dilute hydrochloric acid in long needles melting with decomposition at 255° C. The amine liberated from this crystallized from n. hexane, m.p. 64°–65° C. Only one amino compound was obtained in all experiments.

Methylation of 9-Aminofluorene.—The free amine was shaken up with an excess of sodium hydroxide and dimethyl sulphate, the excess of the latter compound being destroyed at the end of the reaction. The mixture was cooled, extracted with benzene, washed free from alkali and a stream of dry hydrogen chloride was passed. The hydrochloride of the base which was thrown down was recrystallised from an alcohol ether mixture. The free base was obtained by basification and ether extraction. The residual oil after removing ether was purified by distillation under ordinary pressure, the distillate readily solidifying to fine long needles, m.p. 49–50° C. Picrate m.p. 203–04° (yield 10·20%) (*cf.* Ingold and Jessop[3]). The identity of this compound was established by comparison with a specimen prepared by Steven's method.[8]

The tertiary base was converted to the quaternary ammonium compound with methyl iodide and the picrate from this had a melting point 170–75° (*c.f.* next preparation).

Preparation of Fluoryl 9-Trimethyl Ammoniumbromide.—9-Bromofluorene was dissolved in the minimum quantity of acetonitrile and treated with an excess of tri-methylamine, the reaction being carried out at 0° and left overnight. The solution was diluted with ether. An oily substance separated which on keeping overnight at 0° C. solidified in cubical crystals. The salt was filtered, washed with dry ether and appeared pure m.p. 189–90°; Picrate 170–75° C. (yield nearly quantitative).

Nitration of Fluoryl 9-Trimethyl Ammoniumbromide.—Nitration of the bromide invariably led to products with nuclear bromine and the nitro derivatives could be obtained only after conversion of the bromide into other salts.

The bromide (3·04 g.) was converted into the nitrate by reacting with an equivalent amount of silver nitrate, filtered off from the bromide and evaporated to a syrupy consistency when the nitrate crystallised in feathery hygroscopic needles* (m.p. 194° C.). This nitrate was suspended in acetic anhydride (15 c.c.) and treated with 2·5 c.c. concentrated nitric acid (1·42 s.g.) the temperature being maintained below −10° C. and the acid being added dropwise. The reaction mixture was kept at the same temperature for two hours, gradually allowed to rise to room temperature (30° C.) and then heated on the water-bath for one hour. The hot solution was poured into a large volume of water. Small quantities of a white precipitate insoluble in water (fluorenol ?) were filtered off and the clear filtrate treated with sodium picrate. A yellow precipitate was obtained. Purified by recrystallisation from aqueous acetone (with animal charcoal) containing a trace of picric acid, m.p. 225–26° C. (Found: C, 53·1%; H, 4·0%. $C_{22}H_{19}N_5O_9$ requires C, 53·1%; H, 3·8%.)

The same product was obtained by treating the corresponding picrate (1·0 g.) with 5 c.c. of fuming nitric acid, the addition being carried out slowly and the temperature maintained below −10° C. for about two and a half hours. The reaction mixture was allowed to rise slowly to 0° C. and then poured into a large volume of water. No dinitro compound could be isolated (yield > 80%).

The method of Hughes and Kuriyan (*loc. cit.*) for dinitration of sulphonium analogue resulted only in the mono-nitration product.

The position of the nitro group in all these cases was established by comparison with the compound prepared with definitely oriented starting material as follows: 2-nitro 9-bromofluorene was prepared by the method of Anantakrishnan and Hughes (*loc. cit.*) dissolved in acetonitrile and treated with excess trimethyl amine also in acetonitrile solution. The reaction was very rapid (*cf.* Hughes and Kuriyan, *loc. cit.*, for the sulphonium compound). After three quarters of an hour, the quaternary ammonium bromide contaminated with a coloured product crystallised out on addition of a large volume of dry ether. The precipitate was filtered, and washed with ether in which the impurity appeared to dissolve, m.p. 198–200°. (Found: Br, 21·4%. $C_{16}H_{17}N_2O_2Br$ requires Br, 22·9%.) A solution of the bromide in water was treated with an aqueous solution of sodium picrate when the 'Onium picrate separated in fine golden needles (m.p. and mixed melting point with compound obtained above 225–26°).

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* *Note added in proof.*—Slow evaporation of concentrated solutions give tabular prismatic crystals.

Dinitration of Fluoryl 9-Trimethyl Ammonium Salts.—Ordinary conditions of nitration led invariably to mononitro products irrespective of the nitric acid concentration. Only the strongest nitrating agents combined with a moderately high temperature lead to dinitro derivatives.

Fluoryl 9-trimethyl ammonium picrate was treated with a large excess of fuming nitric acid (1 mol. of salt to 70 mols. acid) at room temperature. The temperature shot up to 60° C. and was gradually allowed to cool down. After a few hours, the mixture was cautiously boiled for a short time over the free flame. The clear solution which was somewhat pale in colour was poured into a large volume of water. The picrate separated out as a yellow crystalline powder which was filtered off, washed with water, and recrystallized from dry acetone to which a little picric acid was added. Only one dinitro compound could be isolated, the proportion of the isomer if formed being very low.

The orientation of this was carried out as before. 2:5 and 2:7 Dinitro 9-bromo fluorenes were obtained by the method of Anantakrishnan and Hughes (*loc. cit.*). Reactions of these with trimethyl amine in acetonitrile or nitromethane led to a variety of products. The 'Onium compounds could be obtained in small yields by carrying out the reaction in benzene solution. The coloured products obtained were repeatedly extracted with hot water. The aqueous solutions were evaporated on the water-bath to small bulk. On addition of ether to the concentrated solution, the bromides crystallised out (m.p. of 2:7 Dinitro 9-trimethyl ammonium bromide 225°). (Found: Br, 19·2%. $C_{16}H_{16}N_3O_4$ Br requires Br, 20·3%.) The solutions of the bromides were treated with *neutral* sodium picrate solution. The products were recrystallised from acetone as before. The 2:5 Dinitrofluorenyl 9-trimethyl ammonium picrate was obtained as heavy yellow crystals, m.p. 209–10°.

The 2:7 Dinitro compound was obtained as brownish yellow crystals, m.p. 235–36° C. Mixed m.p. with compound obtained by drastic nitration of unsubstituted salt 236°. (Found: C, 48·7%; H, 3·3%. $C_{22}H_{18}N_6O_{11}$ requires C, 48·7%; H, 3·2%.)

Summary

The nitration of fluoryl-9-trimethylammonium compounds and the orientation of the products is described. It has been found that the best method of obtaining the unsubstituted 'Onium salt is from 9-bromofluorene. The 9-substituent does not appear to have any marked influence on the position of new entrant groups but exerts a noticeable one on the activity

of the nuclear positions. The converse influence of nuclear substituents on the activity of the 9-position is evident.

REFERENCES

1. Hughes and Kuriyan .. *J.C.S.*, 1935, 1610.
2. Huntress and Cliff .. *J. Amer. Chem. Soc.*, 1931, **53**, 2720.
3. Ingold and Jessop .. *J.C.S.*, 1929, 2361.
4. ——— and Wilson .. *Ibid.*, 1933, 1499.
5. Kuhn and Jacob .. *Ber.*, 1925, **58**, 1432.
6. Schmidt and Stutzel .. *Ibid.*, 1908, **41**, 1243.
7. ——— and Wagner .. *Ibid.*, 1910, **43**, 1797.
8. Stevens .. *J.C.S.*, 1930, 2115.

A STUDY OF THE CHEMICAL COMPONENTS OF THE ROOTS OF *DECALEPIS HAMILTONII* (MAKALI VERU)

Part I. Chemical Composition of the Roots

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Decalepis Hamiltonii belongs to the family Asclepiadaceæ of which *Hemidesmus indicus* better known as Indian Sarsaparilla is also a member. It grows largely in South India in the hilly and forest areas of the Western Ghats. The root is cylindrical and measures from 1 to 6 cms. in diameter. It is markedly fleshy and has a strong aroma which is more prominent than that of *Hemidesmus indicus*. It is largely used in making pickles along with limes. The fresh root tastes sweet accompanied by a tingling sensation on the tongue. Barring a note on the isolation of paramethoxysalicylicaldehyde by the steam distillation of the roots[1] no systematic chemical examination of this plant product seems to have been carried out. In the fresh root there is about 82% of moisture; the inner woody core constitutes about 8% and the remaining 92% forms the fleshy portion. The air dried and powdered material can be preserved for a considerable length of time in the absence of a preservative without any deterioration. A description of the extracts obtained by means of various solvents used in succession is given in the experimental part. Since the most considerable portions were extracted by means of petroleum ether and alcohol and the rest did not extract significant amounts, several kilograms of the root were extracted with these two solvents alone and the products studied in detail.

The petroleum ether extract constituted about 3% of the air-dry root and contained all the oily and waxy matter besides certain crystalline compounds. It was at first separated into two main fractions by means of alcohol, (1) the alcohol soluble and (2) the alcohol insoluble portion. The alcohol insoluble fraction was waxy in appearance. After saponification of the wax and careful fractionation of the products, the following substances were obtained: (1) a ketonic-substance melting at 83°, (2) alcoholic

substances belonging to the resinol* group melting between 151–165°, (3) phytosterol mixture melting at about 110° the acetates of which melt between 130–60° and (4) solid and liquid fatty acids. It is possible that the resinols and the phytosterols exist in the wax as esters. From the alcohol soluble portion three definite fractions were isolated. The least soluble fraction (A) consisted mostly of the alcohols of the resinol type contaminated with a little wax. It melted at about 175–85° and simple crystallisation was not enough to purify it. It was therefore subjected to a preliminary saponification before fractional crystallisation. Resinols more or less similar to those contained in the waxy portion were found to be present here also. From a rough estimate the total quantity of resinols was about 17·0 g., whereas the amount of phytosterols existing mostly as esters was about 3·0 g. in 4 kg. of the roots. From the middle fraction (B) melting at about 205–10° could be obtained after repeated crystallisations from ethyl acetate, besides some fractions melting at 210–22°, a definite compound melting at 235–6° having the formula $C_{32}H_{52}O_2$. The most soluble fraction (C) consisted of an essential oil more than 80% of which was found to be para methoxysalicylicaldehyde.

The ordinary reagents that were employed for characterising the sterols such as the Liebermann, the Hesse and the Liebermann-Burchard reagents easily distinguish between the sterols proper and the resinols obtained from the petrol extract. The details are given in the experimental section.

From the alcoholic extract of the root the following substances could be isolated: (1) *Saponins.*—The alcohol extract was concentrated and treated with excess of ether thereby precipitating saponins. (2) *Tannins.*—The alcohol-ether solution was distilled in order to remove the solvents and then diluted with a large volume of water when tannins were precipitated. (3) *Resin acids.*—By extracting the aqueous solution with ether and carefully examining the ether extract a crystalline resin acid melting at 245° and having the composition $C_{22}H_{28}O_{10}$ along with small quantities of an amorphous acid melting at about 180° were obtained. (4) *Inositol.*—The final aqueous solution yielded a precipitate with basic lead acetate from which after removing lead with hydrogen sulphide inactive inositol could be isolated.

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* The term resinol has been used here to indicate tentatively those substances which are alcoholic in nature and which do not give the correct reaction of sterols. Their exact constitutions are being investigated. But since they exhibit similarity with substances of the type of amyrin the use of the term resinol seems to be appropriate.

Experimental

Large quantities of the fresh and fully grown roots of *Decalepis Hamiltonii* were obtained from the Coimbatore district in the month of December. They were cut into thin slices, dried in the sun and stored in well stoppered containers. The material kept very well for over two years without the help of any preservative. When required for use the material was ground to coarse powder and employed.

With a view to determine the moisture content of the fresh root, a representative sample of the roots was shredded by means of a cane shredder and using this material the loss in weight when dried at 100–05° for 3 hours was determined. The moisture was found to be 82% of the fresh root. The woody parts of the roots were separated from the fleshy portion by scraping with a knife and separately weighed. They constituted only 8% of the fresh root.

100 g. of the air-dried powdered root were extracted successively with different solvents. The quantity of each extract and the properties are given below:

1.	Petroleum ether	3·4%
2.	Ether	0·8%
3.	Chloroform	0·8%
4.	Ethyl alcohol	3·7%
5.	Water	2·3%

1. The petroleum ether extract was a brown, sweet smelling waxy mass. It consisted of fatty and waxy matter, some crystalline compounds and the sweet smelling aldehyde, para methoxysalicylicaldehyde. It gave a pink colour with alcoholic ferric chloride.

2. The ether extract was an orange-yellow semisolid mass with a weak bitter taste. It contained some resin acids and gave the same colour reaction with ferric chloride solution as the petrol extract.

3. The chloroform extract was brown in colour and tasted bitter. The alcoholic solution of the extract gave a greenish blue colour with ferric chloride.

4. The alcohol extract was a dark brown semisolid mass. It tasted bitter mixed with a little sweetness. It gave a blue black precipitate with alcoholic ferric chloride. It reduced Fehling's solution thereby indicating the presence of reducing substances. On the addition of water a good amount of an amorphous brown solid was thrown down which gave positive colour reactions for tannins.

5. The water extract did not possess any marked taste. It gave a pale green colour with ferric chloride solution. When an equal volume of alcohol was added to it a copious precipitate of gums and pectins was thrown down. The extract was easily attacked by fungus.

The above extracts were individually tested for the presence of alkaloids with the usual reagents but no alkaloid could be detected.

Extraction of the Roots with Light Petroleum.—

For a complete examination of the root, 4 kg. of the powder were extracted in a big Soxhlet extractor in batches of 1 kg. with petroleum ether (B.P. 60–80°) until further extraction gave no solid matter (about 20 hours per batch). Most of the petrol was recovered from the extract by distillation and the last traces of the solvent were removed by bubbling nitrogen gas. The yellowish brown solid (120 g.) was then boiled with alcohol (200 c.c.) and the mixture allowed to cool down to about 60° when most of the waxy matter solidified. The clear solution was then decanted. More alcohol was added to the solid residue and the process repeated till about a litre of alcohol was employed for the extraction. All the alcohol extracts were collected together. The insoluble waxy material was named (W) and its analysis is described separately. When the alcoholic solution was concentrated to nearly half its bulk and allowed to stand for a day at the room temperature a colourless high melting solid separated out. This weighed about 15 g. and was termed (A). The mother liquor was subsequently slowly concentrated in stages and cooled in the ice chest and the colourless solid material separating out was collected till no more was obtained. The aggregate of this product was designated (B). The final mother liquor left behind was called (C).

Examination of the Fractions of the Petrol Extract.—

Wax (W) (60 g.).—This was a sticky mass melting between 60–70°. It was dissolved in about 50 c.c. of benzene and heated under reflux for about 12 hours with 200 c.c. of N/2 alcoholic potash. The solvents were distilled off as completely as possible, the residue mixed with pumice stone and dried on a steam-bath. The dry material was extracted completely with petroleum ether and acetone in succession. But it was noticed that the petroleum ether had removed all extractable matter and nothing was left for acetone to extract. The petrol extract was washed with water and dried over anhydrous sodium sulphate. This procedure had to be adopted for separating the unsaponifiable matter since the ordinary method using the aqueous suspension gave rise to very difficult emulsions when extracted with petroleum ether.

The petroleum ether extract of the unsaponifiable matter was distilled in order to remove the solvent and the residue was dissolved in about 500 c.c. of hot alcohol. About 3 g. of an amorphous solid (K) came down on cooling; it was filtered and the filtrate was examined separately. The solid (K) was sparingly soluble in ether and alcohol and readily soluble in ethyl acetate. It could be crystallised from alcohol when a large volume of the solvent was employed for the purpose. But final crystallisations (thrice) from ethyl acetate were necessary to render it quite pure. It was thus obtained in colourless hexagonal plates melting at 83–84°. (Found: C, 80·6; H, 13·6%.). When the compound was dissolved in chloroform and concentrated sulphuric acid added, it did not exhibit any colour or fluorescence and gave no colour with the Liebermann-Burchard reagent. When boiled with acetic anhydride and sodium acetate on an oil-bath for 5 hours it remained unchanged. When, however, it was boiled for about 3 hours in alcoholic solution with hydroxylamine hydrochloride and alkali it gave rise to an oxime which could be easily separated from the unchanged ketone by means of the greater solubility of the oxime in alcohol. It was obtained in the form of colourless needles melting at 68°. The nature of this ketonic substance is under investigation.

The filtrate left after the separation of the ketone (K) was concentrated to about half its bulk and treated with 50 c.c. of acetone. This mixture was concentrated and the crystallising solid was obtained in three different fractions: fraction (1) melting between 160–65° (6·5 g.), fraction (2) melting between 155–57° (1·4 g.) and fraction (3) melting between 151–53° (2 g.). All these agreed in properties very closely with similar fractions obtained from component (A). Hence they are described in detail in that connection.

Isolation of Sterols.—The residual mother liquor left after the separation of the above fractions was evaporated to dryness when an orange yellow sticky mass was produced. It was dissolved in a mixture of petroleum ether and alcohol and the solution decolourised using a little animal charcoal. The very pale yellow solution thus obtained was evaporated to dryness and the residue taken up in chloroform. This solution was treated with sufficient amount of alcohol to produce turbidity and allowed to stand in an ice-chest for several days when shining hexagonal plates separated out (1 g.) melting at 105–10°. When a chloroform solution of this substance was boiled with acetic anhydride and a drop of concentrated sulphuric acid added there was a play of colours, pink-blue-green. A chloroform solution of the compound produced blood-red colour with concentrated sulphuric acid with a greenish blue fluorescence. When the mother liquor was evaporated an amorphous

mass giving sterol reactions was obtained. Since ordinary methods of crystallisation failed to yield a crystalline product, the dry mass (2 g.) was acetylated by boiling with acetic anhydride (25 c.c.) and sodium acetate (5 g.) for three hours. The product was treated with 200 c.c. of water and allowed to stand in the cold for a day. The solid that separated out was dissolved in about 100 c.c. of alcohol and cooled in ice. An amorphous semisolid mass soon separated out. The clear alcoholic solution was then decanted and kept in the ice-chest for about 16 hours. A colourless crystalline solid consisting of the acetates was thus obtained melting at 130–60°. It gave the usual sterol reactions. From the melting point of the acetate mixture it may be inferred that the sterol fraction consists of a mixture of stigma and brassica sterols. This point is still under investigation.

Fatty Acids (12 g.).—The soap which had been extracted with petroleum ether and acetone was treated with water and decomposed by means of dilute sulphuric acid. The liberated fatty acids were extracted with ether and the ether distilled off from the extract. The yield of the mixed fatty acids thereby obtained (after drying) was 12 g. When separated by means of Twitchell's lead salt method into alcohol soluble and alcohol insoluble salts and on their subsequent decomposition, it was found to consist of 75% of solid and 25% of liquid fatty acids. The solid acids melted at 80–82° and seemed to consist mainly of higher fatty acids (saponification equivalent 360). The composition of this mixture and that of the liquid fraction is under investigation.

Composition of Fraction A (12 g.).—This colourless solid which melted at about 175–85° appeared to be crystalline but it had no definite shape under the microscope. It dissolved readily in ether, acetone, ethyl acetate and chloroform even in the cold but was sparingly soluble in alcohol. A chloroform solution of the substance gave a yellow colour with concentrated sulphuric acid and developed a greenish-blue fluorescence on standing. When a similar chloroform solution was boiled with acetic anhydride and a drop of concentrated sulphuric acid added (Liebermann-Burchard reaction) a deep pink colour was produced and it lasted for several hours. These reactions are somewhat different from those given by sterols. The crude solid was optically active, $[\alpha]_D^{29}$ being $+61{\cdot}9°$. Since the solid could not be completely purified by simple recrystallisations from the ordinary solvents it was subjected to treatment with N/2 alcoholic potash just as in the case of the wax (W). On cooling the mixture a crystalline mass separated out even in the presence of the alkali. However the whole mixture was evaporated, mixed with pumice stone, dried

and extracted with petroleum ether and acetone. The petrol extracted all the unsaponifiable matter. The extract was washed with water, dried over sodium sulphate and distilled in order to recover the solvent. The residue was dissolved in about 350 c.c. of hot alcohol and allowed to stand for two days at the end of which a colourless crystalline solid (long narrow rods and needles) melting at 175–85° was found to have separated out. It was filtered off, the mother liquor was concentrated and the solid fractions crystallising out were collected in stages. The following 6 fractions were thus obtained and no further crystalline substance was left in the final mother liquor.

Yields and analysis of the fractions

M.P.	Yield	Analysis
1. 175–185°	3·0 g.	C 84·6; H 11·3
2. 160–165°	1·5 „	C 82·7; H 11·6
3. 155–157°	0·8 „	C 83·8; H 11·5
4. 151–153°	0·5 „	C 81·9; H 12·3
5. 135–145°	0·5 „	
6. 130–138°	0·5 „	

The individual fractions exhibited the same solubility in different solvents and the same colour reactions as shown by the crude mixture. The three fractions obtained previously from the wax (W) were found to be similar in composition with the corresponding fractions (2), (3) and (4) above. They gave the same colour reactions (*i.e.*,) a yellow colour with the Hesse's reagent and a pink colour with the Liebermann-Burchard reagent. It was also noticed that there was no depression in melting points when the fractions 1, 2 and 3 from the wax were mixed with the fractions 2, 3 and 4 respectively described above.

Fraction (1) described above was acetylated, as a typical member of this group, by boiling with acetic anhydride and sodium acetate for 3½ hours on an oil-bath. After treatment with a large excess of water the product was crystallised from alcohol-acetone mixture. Two crops of colourless crystals were obtained one melting at 212–18° and the other at 194–98°. With a view to be sure that they were different from the original substance, and that there had been acetylation the acetate fraction melting at 212–18° was analysed. (Found: C, 79·9; H, 10·5%.) It was therefore concluded that there was acetylation and the various fractions consisted of hydroxy compounds of the resinol type.

After the separation of the unsaponifiable matter the remaining soap was dissolved in water and acidified. Only a very small quantity of fatty acids was obtained and hence the fraction (A) consisted mostly of the unsaponifiable matter.

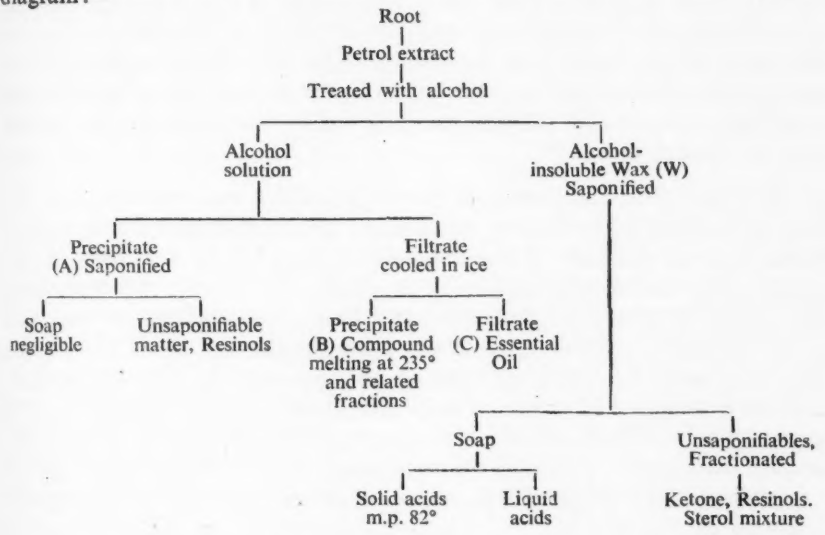
It is interesting to note that the same resinol fractions are obtained from the wax (W) and the fraction (A). It seems probable that they exist both free and in the combined form as esters. The properties of the waxy portion may be due to the existence predominantly of the esters. The high melting point and other characteristics of fraction (A) may be accounted for by their existence in the free form.

Fraction (*B*) (2 g.).—As already mentioned this fraction was easily soluble in ether and hot ethyl acetate and after repeated recrystallisation (6 times) from the latter solvent a small quantity (0·5 g.) of a colourless crystalline (rectangular rods) compound melting at 235–36° was obtained. There was no rise in melting point after further crystallisation. Besides this, fractions melting between 210–22° were obtained. They seemed to contain the same compound mixed with various quantities of impurities because they had the same properties and reactions. The pure substance and also the lower melting fractions gave a pale yellow colour when treated with chloroform and concentrated sulphuric acid and a greenish blue fluorescence slowly developed on standing. A deep pink colour was produced with the Liebermann-Burchard reagent. (Found: C, 82·0; H, 10·7; $C_{32}H_{52}O_2$ requires C, 82·1; H, 11·1%.) The compound was neutral and did not exhibit the properties of a carboxylic acid or a phenol. It did not undergo acetylation when boiled with acetic anhydride and sodium acetate and consequently it did not contain an alcoholic hydroxyl group. It seems to belong to the group of colourless compounds found in the wax (W) and in the fraction (A) since the same colour reactions are given by both but difference seems to exist with respect to the function of the oxygen atoms.

Fraction (*C*).—The final alcoholic mother liquor was distilled in order to recover all the alcohol, the brown oily residue was dissolved in ether and the ether solution dried over anhydrous sodium sulphate. After filtering it was distilled to recover the solvent. About 40 g. of a viscous oily substance was left behind. Though this solidified to a crystalline mass on cooling in a refrigerator it rapidly melted at the room temperature. Hence it was extracted with excess of petroleum ether when a small quantity of a dark viscous liquid was left behind. The petrol solution was decanted and on being concentrated and cooled yielded colourless crystals of paramethoxysalicylicaldehyde. It melted at 42° and no depression in melting point was

noticed when mixed with a synthetic specimen of the aldehyde. It had the characteristic odour and gave pink colour with ferric chloride. The yield of the pure aldehyde was 32 g. amounting to 0·8% of the air-dried root. The coloured viscous material left behind still possessed the smell of the aldehyde but no more of it could be isolated from it by extraction. However when it was dissolved in ether and treated with bromine a small quantity of a bromoderivative melting at 120–21° was obtained. This was identified as the 5-bromoderivative of the aldehyde and hence it was concluded that the resin still contained some amount of the above aldehyde.

The working up of the petrol extract is summed up in the following diagram:—



Extraction with Alcohol.—The root powder which had been exhausted with light petroleum was dried in a current of air and subsequently extracted for about 30 hours with methylated spirits (distilled over lime) in the same apparatus. The alcohol soluble matter was separated into a number of fractions and each fraction examined in detail. The brown extract was concentrated to one-fourth its bulk (500 c.c.) by distillation under reduced pressure. A small quantity of a brown solid (D) separated out and it was removed by filtration. The filtrate was then treated with excess of ether when a dark slimy substance (E) was thrown out. The alcohol ether mixture was again distilled to remove the solvents as far as possible and the residue was treated with a large excess of boiling water. Thereby a considerable

amount of a brown solid (F) was obtained. This was mixed with (D) for purposes of further examination. The aqueous solution was extracted repeatedly with ether and amyl alcohol in succession. The ether extract (G) and the amyl alcohol extract (H) were also examined separately. The final aqueous extract was subsequently treated with neutral and basic lead acetate solutions and these precipitates also were examined.

Fractions (D) and (F):—The solid weighed about 0·7% on the weight of the dry root. It had a mixture of bitter and acid taste. It was packed in a Soxhlet extractor and subjected to successive extraction with petroleum ether, ether, chloroform and alcohol. Petroleum ether and chloroform extracts were negligible. From the ether solution a very small quantity of a crystalline acid melting at 245° could be obtained by adopting the process described in connection with the fraction (G). The alcohol extract gave a green solution with ferric chloride indicating the presence of tannins. It was noted that considerable quantities of the solid now remained unextracted even by alcohol.

Fraction (E).—This was dark brown in colour and very bitter to the taste and swelled considerably on drying. When shaken up with a little water it exhibited plenty of frothing. It was purified by dissolving in dry alcohol (50 c.c.) and precipitating by the addition of a large excess of ether. The process was repeated four times and finally the solid was treated with water. A small quantity of water-insoluble residue gave tests for tannins and the aqueous solution when concentrated on a water-bath yielded a semi-solid mass which could not be crystallised. It gave tests for saponins. The ether alcohol solutions obtained in the course of the purification of the saponin left a small quantity of solid matter on evaporation and this yielded a crystalline acid melting at 245° under the conditions described in connection with the fraction (G).

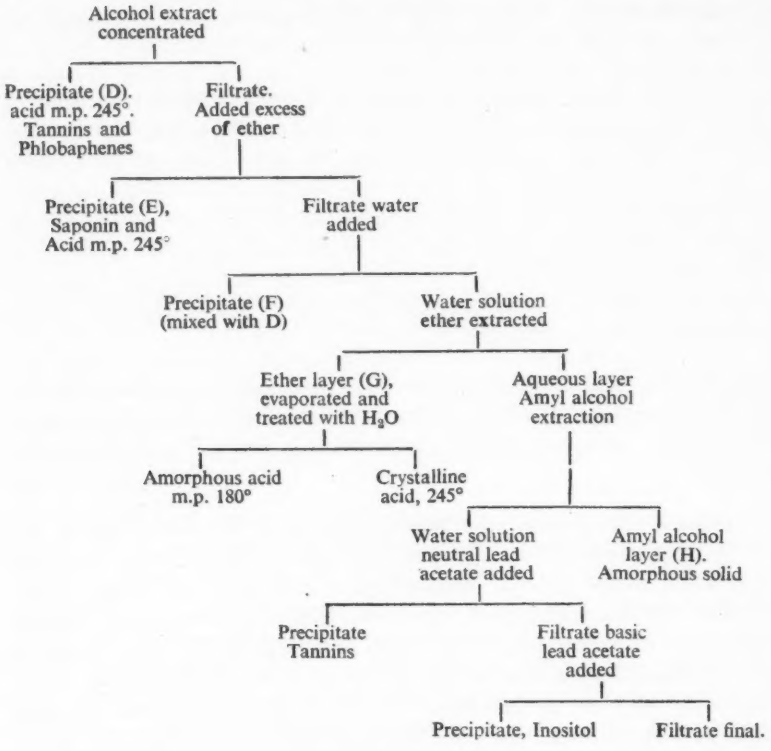
Fraction (G), Ether Extract.—On distilling off the solvent the residue was noticed to have a sweet smell. It gave a greenish blue colour with ferric chloride solution. When treated with ice-cold water it formed a colloidal suspension along with a considerable amount of insoluble brown mass and these were separated. The water suspension was acidified with a few drops of hydrochloric acid and extracted with ether. The solvent was recovered from the ether solution and the residue was treated with a small quantity of water and allowed to stand in the ice-chest for about 12 hours. A yellow crystalline solid (0·5 g.) (plates and rods) melting at 245° was thus obtained. It was filtered and recrystallised from alcohol. The substance was readily soluble in ether and alcohol and aqueous alkali

and was not affected by boiling with 7% hydrochloric acid. (Found: C, 58·8; H, 5·8; and $C_{22}H_{28}O_{10}$ requires C, 58·3; H, 6·2%.)

The insoluble brown solid was dried on a porous plate, dissolved in ether and the ether solution was extracted with aqueous sodium bicarbonate. The alkaline solution was acidified and ether extracted. By repeated transference between bicarbonate and ether and finally evaporating the ether solution an amorphous solid acid melting at about 180° was obtained. It did not give any colour with alcoholic ferric chloride and could not be obtained crystalline. Further extraction of the original ether solution with aqueous sodium carbonate yielded highly coloured amorphous substances from which nothing definite could be obtained.

Fraction (*H*).—The amyl alcohol extract was mainly examined for the existence of glycosides. It was concentrated under reduced pressure and the brown residue examined with various solvents but no crystalline solid could be obtained.

Lead Salts.—The precipitated neutral lead salt was decomposed by means of hydrogen sulphide in aqueous suspension. The aqueous solution on concentration under reduced pressure gave a dark brown mass which gave tests for tannins. The basic lead precipitate however under similar treatment yielded an amorphous solid which dissolved partly in hot absolute alcohol. The insoluble residue was dissolved in a little quantity of water and treated with sufficient alcohol to produce turbidity and allowed to stand, occasionally adding a little alcohol in order to promote crystallisation. After two months a colourless crystalline solid was obtained. It was filtered and washed with alcohol. The impure product was finally recrystallised by dissolving it in a small quantity of water and adding excess of alcohol when clusters of glistening crystals were obtained melting at 221°. It was sweet to the taste and was optically inactive. Its identity with inactive inositol was established with the mixed melting point determination with an authentic sample. The alcohol soluble part of the basic lead salt further contained a little amorphous matter which exhibited the properties of tannins.


Alcohol extract concentrated
Precipitate (D). acid m.p. 245°. Tannins and Phlobaphenes
Filtrate. Added excess of ether
Precipitate (E), Saponin and Acid m.p. 245°
Filtrate water added
Precipitate (F) (mixed with D)
Water solution ether extracted
Ether layer (G), evaporated and treated with H_2O
Aqueous layer Amyl alcohol extraction
Amorphous acid m.p. 180°
Crystalline acid, 245°
Water solution neutral lead acetate added
Amyl alcohol layer (H). Amorphous solid
Precipitate Tannins
Filtrate basic lead acetate added
Precipitate, Inositol
Filtrate final.

Summary

The general chemical composition of the roots of *Decalepis Hamiltonii* has been studied. The petroleum ether extract of the Decalepis roots was found to contain (1) a ketonic substance melting at 83–84°, resinol fractions melting between 130 and 185°, a definite compound of the same group melting at 235–36°, sterols and para methoxysalicylicaldehyde. The subsequent alcohol extract contained besides saponins and tannins a crystalline resin acid melting at 245°, an amorphous resin acid melting at 180° and inactive inositol.

REFERENCE

Rao and Iyengar .. *Perf. Essent. Oil Rec.*, 1923, 14, 300–01.

SYNTHESES IN THE CHAULMOOGRIC ACID SERIES

Part III. Synthesis of *dl*-Hydnocarpic Acid

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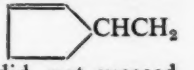
In Part I of this series Bokil and Nargund (1937) described a new synthesis of dihydrohydnocarpic acid, requiring fewer steps than those involved in the method of Noller and Adams (1926). On the lines of the methods developed for the syntheses of dihydro derivatives, Noller and Adams (1926) attempted the synthesis of *dl*-hydnocarpic acid; thus starting with Δ^2-cyclopentene chloride they had prepared the hydroxy compound 
$CHOH(CH_2)_8COOCH_3$. It appears, however, that they did not succeed in eliminating the hydroxy group when they finally declared the subject to have been abandoned (Arvin and Adams, 1928) due to the prior synthesis of *dl*-chaulmoogric acid by Perkins and Cruz (1927). Finally by converting hydnocarpic acid into chaulmoogric acid, Stanley and Adams (1929) indirectly proved the structure of hydnocarpic acid. In spite of these syntheses, however, the direct synthesis of hydnocarpic acid by a more suitable method was thought to be a sufficiently inviting problem, especially in view of the fact that the excellent methods of syntheses in this series, developed by Adams and his co-workers, seemed to have proved unworkable for its synthesis. Moreover, the above methods, and the method of Perkins and Cruz (*loc. cit.*) involved the use of a substance (cyclopentadiene) of most uncommon occurrence and—to put it in the words of the latter authors "a substance (Δ^2-cyclopentenyl chloride) of extraordinary reactivity which renders unusual precautions necessary in its preparation and handling," although it may form an excellent starting material.

The new method for the synthesis of hydnocarpic acid and its homologues, indicated by the present authors in Part I (*loc. cit.*)—though it depends upon the availability of the required halogen substitution products of fatty acids, as is also the case in Perkins and Cruz's synthesis—has the added advantage that it avoids the use of Δ^2-cyclopentenyl chloride. The first member of the series—Δ^2-cyclopentenyl carboxylic acid—was synthesised

according to the methods suggested in Part I, and has already been reported in Part II by Bokil and Nargund (1940). It was at first thought possible to synthesise *dl*-hydnocarpic acid from cyclopentanone-2-ω-undecylic acid or its ester, by similar methods in accordance with the following scheme:—

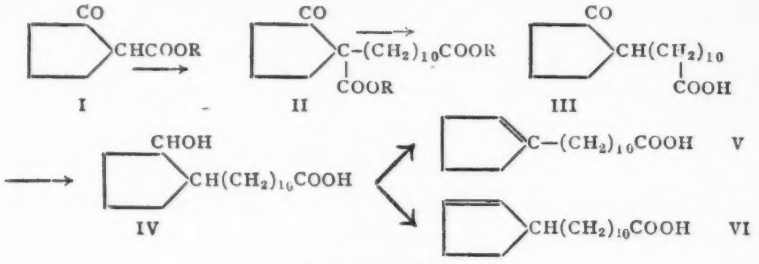


Diagram No. 1

The free acid (III) was treated with sodium and alcohol according to the method used by R. Hirst (*cf.* Rapson and Robinson, 1935) for the reduction of cyclopentanone-2-β-propionic acid. Treatment with phosphorus pentoxide of the resulting product—which could not be purified—gave, however, negative results. A modification of the above method was then tried in which the possibility of the formation of the isomeric product (V) could be avoided, and the double bond could be fixed in the required position in accordance with the following scheme :—

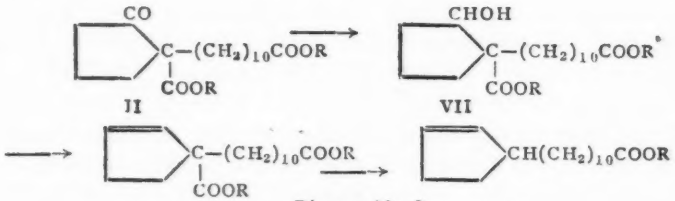


Diagram No. 2

Ethyl cyclopentane-2-one-1-carbethoxy-1-ω-undecylate (II) was treated with large excess of sodium amalgam in aqueous alcoholic solution. As in the first case, the extent of reduction could not be determined because of the nondistillability of the product; hence it was directly treated with phosphorus pentoxide in benzene. From the resulting product, only the keto acid (III—semicarbazone reaction), and a small quantity of a tribasic acid (m.p. 89–90°) were isolated, the latter being identified later, as α-α'-δ-tricarboxy-*n*-tetradecane (IX). It was, therefore, evident that the keto acid was not reduced to any appreciable extent, it being merely decomposed during subsequent treatment.

The object, however, was finally achieved by a further modification of the above method. The keto ester (II) was decomposed by alcoholic potash (containing the phase C_2H_5OK) into a tricarboxylic acid—α-α′-δ-tricarboxy-*n*-tetradecane (IX), m.p. 92–93°—and the ester of this was cyclised into ethyl cyclopentane-2-one-1-carbethoxy-3-ω-undecylate (X—*cf.* Dieckmann, 1901). This keto ester was reduced with a very large quantity of sodium amalgam in aqueous alcoholic solution, till it gave no bluish violet colour with alcoholic ferric chloride solution. The hydroxy ester (XI) could not be purified; it was hydrolysed and the resulting hydroxy dibasic acid was boiled with acetic anhydride. This yielded, in addition to a small quantity of the tribasic acid (IX), a mixture of unsaturated dibasic acid (XII), and an unsaturated monobasic acid—*dl*-hydnocarpic acid (VI), by the simultaneous decarboxylation of the above dicarboxylic aicd (*cf.* Wallach, 1907):—

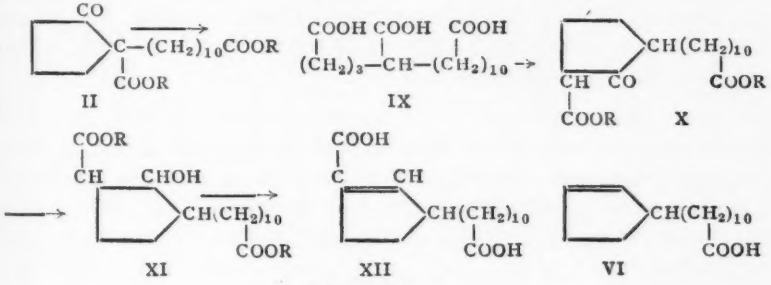


Diagram No. 3

The separation of the two unsaturated acids was conveniently effected through their barium salts—the salt of the monobasic acid being soluble in hot alcohol. Power and Barrowcliff (1905) took advantage of the same method in separating active hydnocarpic acid from the rest of the acids. The monobasic acid thus obtained melted at 46–47°. It was at first purified from 80 per cent. alcohol at 0° (m.p. 53–54°) and then recrystallised several times from light petroleum at 10–15°. It now melted at 58–59°, and was identified by the melting point of its mixture with an authentic sample (m.p. 58·5–59·5°—prepared from the "ethyl hydnocarpate oil" of B.D.H quality) which did not change. The amides were also prepared from both the synthetic and the natural active hydnocarpic acids, according to the method of Hinegardner (1933), and identified by mixed melting point. This is in agreement with the observation of Hinegardner (*loc. cit.*) who racemised active hydnocarpic acid and showed that the *dl*-acid (melting point same as that of the active acid) and the active acid do not show a depression in their melting point when mixed together. Their amides also showed the same behaviour.

Experimental

Ethyl cyclopentane-2-one-1-carbethoxy-1-ω-undecylate (II) was prepared as described in Part I (*loc. cit.*).

Preparation of the tribasic acid.—α-α′-δ-Tricarboxy-*n*-tetradecane (IX):—The above keto ester (35 gm.) was mixed with an alcoholic solution of caustic potash (16 gm. in 10 c.c. water made up to 50 c.c. by absolute alcohol); heat was evolved and the mixture solidified within a minute. It was then heated on water-bath for two hours, alcohol distilled off and the residue evaporated to dryness. A concentrated solution of this in water was extracted with ether and acidified carefully with concentrated hydrochloric acid under cooling; the white precipitate was filtered at the pump and dried without washing. The substance was soluble in water and was found to be an acid potassium salt. For purposes of analysis it was purified by precipitating it from its concentrated solution in water by alcohol. (0·7362 gm. gave 0·1751 gm. K_2SO_4 ; K = 10·7 per cent. $C_{17}H_{29}O_6K$ requires K = 10·6 per cent.)

Complete decomposition of the above salt gave a solid acid (yield 25 gm.) which was insoluble in benzene, petroleum ether and chloroform, and soluble in ether, alcohol and ethyl acetate. It separated in the form of white powder from a mixture of ether and petrol—m.p. 92–93° (sintering at 90°). It also crystallises from dilute ethyl alcohol (about 30 per cent. strength) in the form of fine short silky needles—m.p. 92–93°. (Found: C, 61·5; H, 9·1 per cent.; Equit. wt., 110·5; $C_{17}H_{30}O_6$ requires C, 61·9; H, 9·1 per cent.; Equit. wt., 110.)

Preparation of the triester.—The usual Fischer Speier method of esterification gave a low yield of the triester; it was therefore, prepared by the silver salt method—a thick colourless liquid which distilled between 250–60°/5 mm. Comparatively a large amount of the ester gets decomposed during distillation; 37 gm. of the acid yielded 28 gm. of the purified ester, *i.e.*, 65 per cent. of the theory. (Found: C, 66·3; H, 10·4 per cent.; $C_{23}H_{42}O_6$ requires C, 66·7; H, 10·1 per cent.)

Cyclisation of the above triester—formation of ethyl cyclopentane-2-one-1-carbethoxy-3-ω-undecylate (X).—Finely powdered sodium (2·6 gm.) was placed in 100 c.c. dry benzene in a flask fitted with a reflux condenser; the triester (41·4 gm.) was added and the mixture heated on a boiling water bath for an hour and a half, when a yellowish-red, transparent jelly-like mass of the sodium salt separated. To complete the reaction the mixture was heated further for five hours, cooled and decomposed by ice-cold 10 per cent. hydrochloric acid solution. Benzene layer was washed, dried

and the solvent removed—yield 36·5 gms. it gave an intense bluish-violet colouration with alcoholic ferric chloride. It could not be distilled even at very low pressure (2 mm.); only low boiling portions were distilled off upto 200°. The dark red liquid in the flask was taken up with ether to remove some sediment collected at the bottom, and ether removed—yield 26 gm. It gave a semicarbazone crystallising from alcohol in white flocculent powder—m.p. 146–47° (clear at 150°). (0·2123 gm. gave 17·1 c.c. of N_2 at 30° and 758 mm. pressure. Found: N, 10·1 per cent.; $C_{22}H_{39}O_5N_3$ requires N, 9·9 per cent.)

Reduction of the above ester.—The ester in lots of 5 gm. each in 60 c.c. of alcohol and 15 c.c. of water, was treated with 225 gm. of 4 per cent. sodium amalgam in a strong current of carbon dioxide during 24 hours; then it gave no colouration when tested with alcoholic ferric chloride. Alcohol was then removed and the substance recovered; yield 18 gm. from 25 gm. of the keto ester. It could not be purified by distillation even under reduced pressure.

Hydrolysis of the hydroxy ester by methyl alcoholic potassium hydroxide was carried out in the usual manner. The acid recovered (yield 14 gm.) was used for dehydration without further purification.

Dehydration of the above hydroxy dibasic acid.—The acid (13 gm.) was mixed with acetic anhydride (22 c.c.) and the mixture gently boiled on a sand-bath for three hours. Water was then added, steam-distilled to remove acetic acid and the substance recovered by ether—yield 12 gm., a thick dark brown liquid which quickly decolourised bromine in chloroform. Titration of the crude product (equivalent weight = 175) indicated that the original crude acid mixture may contain about 25 per cent. of *dl*-hydnocarpic acid. The crude acid mixture was dissolved in alcohol (100 c.c.) and neutralised by a saturated solution of barium hydroxide (litmus reaction). This was heated on water-bath and the insoluble salt separated (A). The alcoholic solution was concentrated on water-bath to 50 c.c. and the flocculent precipitate obtained on cooling was separated and dried (B). 10·5 gm. of the dehydrated product yielded 5 gm. of soluble salt (B), and 11·5 gm. of the insoluble salt (A).

Isolation of the dl-*hydnocarpic acid from B* (VI).—The acid recovered in the usual way by decomposing the barium salt (5 gm.) was a pale yellow sticky solid, m.p. 46–47°—yield 3·5 gm. It was first treated with light petroleum to remove the slight quantity of unsaturated dibasic acid it contained—the dibasic acid is insoluble in petrol. The recovered acid was converted into methyl ester and distilled, b.p. 175–80° at 8–9 mm. Shriner

and Adams (1925) give the boiling point of methyl dextro hydnocarpate as 182–83° at 10 mm. The ester was hydrolysed and the acid recovered was crystallised first from 80 per cent. alcohol at 0° (keeping overnight) when it melted at 53–54°. It was then twice recrystallised from light petroleum (b.p. 40–60°) at 10–15° when it had m.p. 58–59°. (Found: C, 76·5; H, 11·0 per cent.; Equit. wt., 251·4; Calculated for $C_{16}H_{28}O_2$, C, 76·2; H, 11·1 per cent.; Equit. wt., 252. Found: iodine number (Hanus) = 99·1; Theoretical value = 100·7.)

The amide of the above acid—prepared by the method of Hinegardner (1933)—was crystallised from petrol and melted at 109–110°.

Isolation of (3-*carboxy*-Δ^2-*cyclopentenyl*-1)-*ω*-*undecylic acid* (XII).—The insoluble barium salt (11·5 gm.) was decomposed with hydrochloric acid and the acid recovered in the usual manner, when it was obtained as a brown sticky solid (5 gm.). Its equivalent weight indicated it to be a mixture. It was soluble in alcohol, ether, acetic acid and ethyl acetate, but insoluble in benzene and petrol. It gave turbid solution in chloroform. The whole of it was treated with chloroform and filtered from a small amount of insoluble substance which was identified as α-α′-δ-tricarboxy-*n*-tetradecane by mixed m.p. The substance recovered from chloroform was converted into the ethyl ester and distilled—b.p. 240–70° at 6–7 mm., $D_4^{26} = 0{\cdot}9897$ $N_D^{26} = 1{\cdot}45247$. The acid obtained by hydrolysing the above ester crystallised in colourless granules from a mixture of petrol and ether, m.p. 82–83° (sintering at 79°). It did not decolourise Br_2 in $CHCl_3$. (Found: C, 68·6; H, 9·5 per cent.; Equit. wt., 147·2; $C_{17}H_{28}O_4$ requires C, 68·9; H, 9·4 per cent.; Equit. wt., 148.)

We thank Dr. M. S. Shah, Head of the Chemistry Department, Gujarat College, Ahmedabad, for facilities.

Summary

1. Synthesis of *dl*-hydnocarpic acid has been effected for the first time and described.

2. The method developed for its synthesis is a simple one and capable of being used as a general method for the synthesis of compounds containing Δ^2-cyclic groups.

REFERENCES

Arvin and Adams .. *J.A.C.S.*, 1928, **50**, 1792.

Bokil and Nargund .. *Jour. Univ. Bom.*, 1937, **2**, 93.

———— .. *Proc. Ind. Acad. Sci.*, 1940, **11**, 409.

Dieckmann .. *Annalen*, 1901, **317**, 26–107.

Hinegardner .. *J.A.C.S.*, 1933, **55**, 2831–34.

Noller and Adams .. *Ibid.*, 1926, **48**, 2445.

———— .. *Ibid.*, 1926, **48**, 1080–89.

Perkins and Cruz .. *Ibid.*, 1927, **49**, 1070.

Power and Barrowcliff .. *J.C.S.*, 1905, 888.

Rapson and Robinson .. *Ibid.*, 1935, 1543.

Shriner and Adams .. *J.A.C.S.*, 1925, **47**, 2737.

Stanley and Adams .. *Ibid.*, 1929, **51**, 1515.

Wallach .. *Annalen*, 1907, **353**, 286.

A CLASSICAL LIMIT OF HEAVY HOMOGENEOUS SPHERICAL MASSES

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In a recent investigation about highly collapsed stars with dense neutron cores having small radius (10^6 cm.) and exceedingly high density (10^{14} g. cm.$^{-3}$) F. Zwicky[1] has considered the classical treatment of proper and effective masses of material spheres. His conclusion is that, gravitation being a 'co-operative phenomenon', the classical theory cannot effectively bring out the distinction between the two kinds of mass even with the help of Einstein's familiar relation,

$$E = Mc^2 \tag{1}$$

Here M is the mass equivalent of the energy E and c is the velocity of light. The object of this note is to show that the Newtonian theory is powerful enough to bring out the distinction between proper and effective masses unambiguously. It is achieved by deriving the formula (7) from first principles. It is not at all suggested that the formula so derived should be used in preference to the corresponding relativistic formula in considerations of heavy masses. The new formula has an interest of its own as it gives an upper limit on the effective mass of a homogeneous sphere which is similar to Schwarzschild's limit. Incidentally, one finds that Volkoff's[2] solutions for a material sphere which give arbitrarily large masses and radii are either mathematical abnormalities, being without Newtonian analogues, or physically significant inasmuch as they show the superiority of general relativity over the other theory.

Consider first a homogeneous sphere of terrestrial dimensions and weight. For in this case one does not go very much astray in taking the conventional definition of homogeneity; also the difference between the proper and effective masses is negligible. If ρ is the density and a the radius the proper mass is supposed to be M:

$$M = \frac{4\pi}{3} \rho a^3 \tag{2}$$

The gravitational potential energy is

$$-\frac{3}{5}\frac{M^2}{a} G, \tag{3}$$

where G is the constant of gravitation and hence on using (1) the effective mass may be stated as M′:

$$M' = M - \frac{3}{5}\frac{M^2}{a}\frac{G}{c^2}. \tag{4}$$

As Zwicky has pointed out the formula (4) is inaccurate and very misleading for large condensed masses such as the supernovæ. The inaccuracy arises through ignoring the distribution of the mass equivalent of the gravitational potential energy the magnitude of which, in its turn, is dependent upon the nature of distribution itself.

The difficulty envisaged by Zwicky can be surmounted by discussing the whole question from a more fundamental standpoint. We will discuss the case of a homogeneous sphere although the same argument can be pursued *mutatis mutandis* for a more complicated distribution. In an idealized case one may consider a flat space-time populated by particles of atomic dimensions each of the same size and mass m. Each particle is supposed to be outside the spheres of influence of all others so that it satisfies Newton's first law. To avoid the complication of mass varying with velocity all the particles may be supposed to be at rest. The mass of a particle is then the pull of the rest of the universe on it and it is defined as its proper mass for that state. Let a homogeneous sphere of radius r be built up in the same space-time frame so that the number of particles per unit volume is constant, being n. Obviously it will not be right to say that the effective density or mass per unit volume of the sphere is mn which is really the proper density. Let m' be the average effective mass of a particle in the sphere of radius r. Similarly let $m' + \delta m'$ be the average effective mass when the spehre is of radius $r + \delta r$. In building up the shell of thickness δr the gain in proper mass is

$$4\pi\gamma^2\delta\gamma mn,$$

while the loss due to the gravitational energy* is

$$\frac{4\pi r^2 m'n\,G}{3c^2}\,4\pi r^2\,\delta r\,mn$$

* It is important to recognise that this loss is

$$\frac{4\pi r^2\, m'n\ G}{3c^2}\ .\ 4\pi r^2\,\delta r\,mn \tag{A}$$

and not

$$\frac{4\pi r^2\, mn\,G}{3c^2}\cdot 4\pi r^2\,\delta r\,mn \tag{B}$$

This distinction is in fact the crucial point of the present paper. The particles, $4\pi r^2\,\delta rn$ in number are brought from infinity to the surface of a sphere of radius r. The sphere has the proper mass $4\pi\ r^2mn/3$ and the effective mass $4\pi r^2m'n/3$. In calculating the gravitational potential of the

Hence we have

$$\frac{4\pi}{3}(r+\delta r)^3(m'+\delta m')\,n=\frac{4\pi}{3}r^3m'n+4\pi r^2\,\delta r\,mn-\frac{4\pi r^2}{3c^2}m'n\,\mathrm{G}\cdot 4\pi r^2\,\delta r\,mn,$$

or

$$4\pi r^2\,\delta r\,m'n+\frac{4\pi r^3}{3}\delta m'n=4\pi r^2\delta r\,mn-\frac{4\pi r^2}{3c^2}m'n\,\mathrm{G}\cdot 4\pi r^2\delta r\,mn,$$

so that

$$\frac{r}{3}\frac{dm'}{dr}=m-m'-mm'nk\,r^2, \tag{5}$$

where

$$\mathrm{K}=\frac{4\pi\,\mathrm{G}}{3c^2}. \tag{6}$$

Solving (5) we get

$$m'=m-\frac{1}{r^3}\,e^{-\frac{3k\,mn}{2}r^2}\int_0^r 3k\,m^2r^4n\,e^{\frac{3k}{2}mnr^2}\,dr \tag{7}$$

If we put

$$\frac{3k\,mn}{2}=\lambda,$$

$$m'=m-\frac{2\lambda m}{r^3}\left[\frac{r^5}{5}-\frac{2}{35}\lambda r^7+\frac{4}{315}\lambda^2r^9\cdots\right]. \tag{8}$$

With

$$\mathrm{G}=6\cdot66\times10^{-8}\ \mathrm{g.^{-1}\,cm.^3\,sec.^{-2}}$$

and

$$c=3\times10^{10}\ \mathrm{cm.\,sec.^{-1}}$$

$$\mathrm{K}=3\cdot1\times10^{-28}\ \mathrm{g.^{-1}\ cm.} \tag{9}$$

Hence even if a very high value is chosen for the density mn say,

$$mn=10^{14}\ \mathrm{g.cm.^{-3}} \tag{10}$$

we find

$$\lambda=4\cdot6\times10^{-14}\ \mathrm{cm.^{-2}} \tag{11}$$

The successive terms of the series in (8) thus fall off very rapidly. Denoting the effective density by ρ' and the proper density by ρ, we have

$$m'n\equiv\rho'=\rho-\frac{3\mathrm{K}}{r^3}\rho^2\left[\frac{r^5}{5}-\frac{2}{35}(3\,\mathrm{K}\rho)\,r^7+\frac{4}{315}(3\mathrm{K}\rho)^2\,r^9+\cdots\right] \tag{12}$$

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sphere at its surface it is the latter that must be used. The proper mass has no meaning for dynamical or kinematical purposes: it merely represents the sum of the masses of the constituent particles when their mutual interactions are neglected, the gravitational mass of a sphere is what is called the effective mass and hence we have to choose (A) in place of (B). The distinction between effective and proper masses, which arises through interaction, could not be logically maintained if (B) were the correct expression.

The relation between the effective mass M′ and the proper mass M of a homogeneous sphere of radius r follows from (12):

$$M' = M - \frac{3M^2G}{r^6c^2}\left[\frac{r^5}{5} - \frac{2}{35}\left(\frac{3\,M}{r^3}\frac{G}{c^2}\right)r^7 + \frac{4}{315}\left(\frac{3\,M}{r^3}\frac{G}{c^2}\right)^2 r^9 \cdots\right]$$

or

$$M' = M - \frac{3\,M^2G}{5\,c^2r} + \frac{18}{35}\frac{M^3G^2}{c^4r^2} - \frac{12}{35}\frac{M^4G^3}{c^6r^3}\cdots. \tag{13}$$

For the sake of clarity it may be stated that

$$M' = \frac{4\pi}{3}\rho' r^3,\ M = \frac{4\pi}{3}\rho r^3. \tag{14}$$

Although ρ' is a function of r its definition allows us to connect it with M′ in the same manner as ρ with M.

For a given proper density ρ we can determine from (7) the maximum value of the effective mass M′. When $\frac{dM'}{dr} = 0$,

$$r^3\frac{d\rho'}{dr} + 3\,r^2\rho' = 0$$

or

$$\frac{r}{3}\frac{dm'}{dr} + m' = 0 \tag{15}$$

Therefore, from (5), we get

$$\frac{4\pi G r^2 m' n}{3\,c^2} = 1 \tag{16}$$

or

$$\frac{M'G}{c^2} = r \tag{17}$$

The Schwarzschild limit is given by

$$\frac{M'G}{c^2} = 2\,r, \tag{18}$$

which may be compared to (17). The classical limit has numerical consequences of the same order as the other.

When Liapounoff[3] obtained his celebrated result that a gravitating homogeneous liquid assumes a spherical form in free space, the gravitational energy being a minimum for the sphere, this distinction between proper and effective masses was unknown. There is reason therefore to expect that his result is not valid for large masses. Bodies of the massiveness of the nebulæ (10^{10} ⊙ or 10^{43} g.) are not at all spherical but largely flat. One is tempted to link this empirical fact with the classical result that a homogeneous

sphere which is being built up with proper density ρ has an effective mass increasing with radius till (17) or its equivalent,

$$\rho' = \frac{3}{4\pi}\left(\frac{c^2}{G}\right)^3 \frac{1}{M'^2} \tag{19}$$

is reached after which the effective mass diminishes with radius. If the spherical form can be preserved only at the cost of effective mass when the critical stage in the building-up process is reached it is not so surprising that the heaviest objects of the universe, the nebulæ, appear as flat bodies with central cores. It is interesting to note from (19) that for M′ of the order of an average nebular mass, ρ' is of the order of unity.

Summary

It is shown that the classical theory effectively brings out the distinction between the effective and proper masses of a homogeneous sphere. The formula derived to clarify this point leads to an upper limit on the effective mass of a sphere which is analogous to Schwarzschild's. The bearing of the limit on the flatness of nebulæ is pointed out.

REFERENCES

1. Zwicky, F. .. *Phys. Rev.*, 1939, **55**, 729.
2. Volkoff, G. M. .. *Ibid.*, 1939, **55**, 413.
3. Appell .. *Mechanique Rationelle, tome quatrieme*, 1921, 37.

THE LEAD RATIO OF A CRYSTAL OF MONAZITE FROM THE GAYA DISTRICT, BIHAR

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The desirability of determining the 'lead ratio' of a radioactive mineral to estimate its age, and hence that of the formation where it occurs, need not be enlarged upon. So far no precise determination of the lead ratio of any Indian mineral has been made. W. R. Criper[1] in 1902 analysed a specimen of pitchblende of unknown quality from Singar, Gaya district, Bihar, but his data cannot be used in calculating the lead ratio, because the thorium content of the mineral was not determined, thorium being present in many pitchblendes and sometimes in quantities up to 10 per cent. or more. Further the sample analysed by Criper contained 0·35 per cent. P_2O_5 and this suggests that perhaps the sample was contaminated with some of the alteration product of the mineral; for Tipper[2] has observed that the alteration product of the pitchblende of the locality reacts strongly for phosphates, whereas usually phosphates are present in pitchblendes only in traces, if at all.[3] Later Holmes[4] analysed a good sample from the same locality, but his analysis also suffers from the defect that thorium was not estimated.

Holmes used Criper's and his own analyses and, assuming that the specimens analysed contained 11·6 per cent. thorium, found that the lead ratios deduced from Criper's and from his own data were 0·12 and 0·13 respectively. The lead ratio of the pitchblendes of this locality is regarded by him to lie between these two values. In his assumption that the thorium contents of the specimens were of the order of 11·6 per cent. he relied on an analysis of pitchblende by Tipper.[2] This is hardly justifiable, as Tipper's specimen was very much altered (that is, mixed with uranium ochre) and Tipper's analysis of uranium ochre shows a higher content of thorium (including the rare earths) than the pitchblende. Further, from a glance at Criper's analysis it is obvious that his specimen could not have contained so much as 11·6 per cent. thorium as in his analysis iron, aluminium and 0·35 per cent. P_2O_5 together equal to 3·35 per cent. of the constituents.

The lead ratios deduced from Criper's and Holmes's analyses (thorium not being taken into account) are 0·128 and 0·138.

From the above, the desirability of a precise determination of the lead ratio of a mineral from this area becomes apparent. Good crystals of monazite said to have been collected from the Gaya district, but from an unspecified locality, were forwarded by Mr. B. Chuckravarti of the National Coal Co., Giridih, to Dr. P. B. Sarkar of the University College of Science, Calcutta, and we chose this mineral for determining its lead ratio. After Fenner's work on the monazite from Brazil[5] and from Portland, Connecticut,[6] there is little room for doubt as to the reliability of the age calculations made from the analyses of this mineral.

The specimen at our disposal seemed to be unaltered, having a bright resinous lustre on fractured surfaces and having only slight yellowish incrustations at places on the surface. Its colour was reddish brown and its specific gravity 5·16. It had no streak and its hardness was greater than 5, as its surface could not be scratched with a sharp knife. When broken up, the small pieces appeared homogeneous and unaltered when examined under a pocket lense.

For analysis a few fresh-looking pieces of the mineral were selected and purified from any possible traces of alteration product with 1 : 3 nitric acid as suggested by Fenner.[5]

Lead, uranium and thorium were estimated in separate portions following the procedure given by Fenner,[7] with slight modification in the case of thorium. The thorium was precipitated three times with hydrogen peroxide from a neutral nitrate solution, but still the precipitate was not absolutely white, so we purified it by precipitating it once with *m*-nitrobenzoic acid.[8] As regards the estimation of uranium we found that the separation of iron and uranium as ferrocyanide in acid medium was rather tedious, as the precipitate settles down only after a long time (about twelve hours) and even then it has a tendency to pass into the colloidal state; the filtration of the precipitate requires filter-paper pulp and is slow, adequate washing being thus difficult. The method for the estimation of lead was satisfactory.

Analysis of Specimen of Monazite from Gaya District, Bihar

	Per cent.
SiO_2	1·56
P_2O_5	27·22
Al_2O_3	1·20
SnO_2	Nil
Fe_2O_3	0·44
TiO_2	Nil
R_2O_3	55·87 (R = Rare Earths)
(*Ce_2O_3*	*22·00*)
(*Y_2O_3*	*1·15*)
ThO_2	12·00
(*Th*	*10·54*)
U_3O_8	0·2677
(*U*	0·2270)
PbO	0·5331
(Pb	0·4949)
CaO	0·83
MgO	0·09
C	Present
Mn	Trace
Na_2O, K_2O ..	Nil
Loss at 110° C. ..	0·15
at 900°C. ..	0·48
	100·64

$$\text{Pb ratio} = \frac{\text{Pb}}{\text{U} + \cdot 36\,\text{Th}} = 0 \cdot 123$$

$$\text{Approximate age} = \frac{\text{Pb}}{\text{U} + \cdot 36\,\text{Th}} \times 7600 \text{ million years}$$

$$= 935 \text{ million years.}$$

$$\text{Corrected age} = \text{Approx. age} \times \left(1 - \frac{x}{2} + \frac{x^2}{3}\right) = 875 \text{ million years}$$

$$\text{where } x = 1 \cdot 155 \frac{\text{Pb}}{\text{U} + \cdot 36\,\text{Th}}.$$

The lead ratio obtained from the monazite points[9] to an age corresponding to the uppermost limit of the Middle Pre-Cambrian for the

pegmatite, where this and other radioactive minerals occur. The view of Sir L. L. Fermor[10] that these pegmatites belonged to the post-Dharwar intrusives of India is supported by the lead ratio obtained here. These pegmatites of Gaya may thus be considered as the last phase of igneous activity in post-Dharwar but pre-Cuddapah times.

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REFERENCES

1. See Holland, T. H. .. *Mem. Geol. Sur. Ind.*, 1902, **34**, 31.
2. Tipper, G. H. .. *Rec. Geol. Surv. Ind., L.*, 1919, 256.
3. Doelter *Handbuch der Mineralchemie*, 1929, **4**, (11).
4. Holmes, A. .. *Quart. Jour. Geol. Soc.*, 1918, **74**, 31.
5. Fenner, C. N. .. *Amer. Journ. Sci.*, 1928, (5) **16**, 382.
6. ———— .. *Ibid.*, 1932, (5), **23**, 327.
7. ———— .. *Ibid.*, 1928, (5), **16**, 369.
8. Neish .. *J. Am. Chem. Soc.*, 1904, **26**, 780.
9. Holmes, A, and Lawson, R. W. *Amer. Journ. Sci.*, 1927, **15**.
10. Fermor, L.L. .. *Jour. A.S.B., N.S.*, 1919, **15**, 170.

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